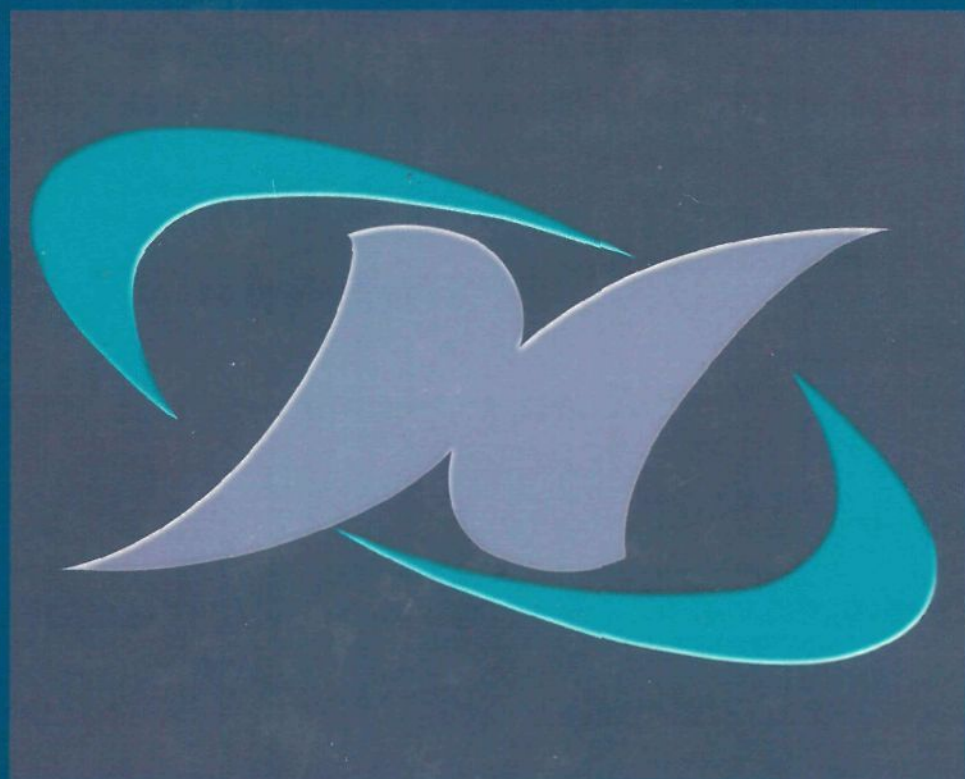


Physics, Chemistry and Application of Nanostructures

Reviews and Short Notes to NANOMEETING-2001



Editors

V. E. Borisenko
S. V. Gaponenko
V. S. Gurin

World Scientific

Physics, Chemistry and Application of Nanostructures

Reviews and Short Notes to NANOMEETING-2001

This page is intentionally left blank

Physics, Chemistry and Application of Nanostructures

Reviews and Short Notes to NANOMEETING-2001

Minsk, Belarus

22— 25 May 2001

Editors

V. E. Borisenko

Belarusian State University of Informatics and Radioelectronics

S. V. Gaponenko

Institute of Molecular and Atomic Physics

V. S. Gurin

Belarusian State University



World Scientific

Singapore • New Jersey • London • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 912805

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

PHYSICS, CHEMISTRY AND APPLICATION OF NANOSTRUCTURES

Reviews and Short Notes to NANOMEETING-2001

Copyright © 2001 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 981-02-4618-8

Printed in Singapore.

INTERNATIONAL CONFERENCE

NANOMEETING-2001

Minsk, Belarus, May 22-25, 2001

ORGANIZERS

Belarusian State University of Informatics and Radioelectronics
(Minsk, Belarus)

and

Le Centre de Recherches sur les Mécanismes de la Croissance Cristalline
(Marseille, France)

SPONSORS

European Commission

INTAS

MOTOROLA

Travelink Invest

Ministry of Education of Belarus

Academy of Sciences of Belarus

Basic Research Foundation of Belarus

INTERNATIONAL ORGANIZING COMMITTEE

V. E. Borisenko – Co-chairman	(Belarus)
F. Arnaud d'Avitaya– Co-chairman	(France)
L. J. Balk	(Germany)
E. V. Buzaneva	(Ukraine)
J. Derrien	(France)
S. V. Gaponenko	(Belarus)
N. Koguchi	(Japan)
B. W. Licznarski	(Poland)
L. W. Molenkamp	(Germany)
S. Ossicini	(Italy)
K. A. Valiev	(Russia)

BELARUSIAN NATIONAL ORGANIZING COMMITTEE

V. I. Strazhev - Chairman
M. P. Batura
A. I. Belous
V. E. Borisenko
V. S. Gurin
F. F. Komarov
A. A. Leshok
N. M. Olekhnovich

FOREWORD

Dear Reader,

You open the book, which contains invited reviews and short notes of contributions to *NANOMEETING-2001*. This Conference is the first international forum of scientists, studying physics and chemistry of nanostructures, of the XXI-st century. It is for main objective helping the development of nanotechnology and promoting nanostructures for applications in modern information and communication technologies. Impressing results of the last century are summarized in the review papers while new challenges of the XXI-st century are arising from the other original contributions. It is evident that even 100 years after the birth of Quantum Mechanics*, we are still learning more and more about interaction between light and electrons in matter. The Constitution of what, we call “nanoworld”, is formed by quantum effects.

The papers in the book are arranged in traditional sections: Physics of Nanostructures, Chemistry of Nanostructures, Nanotechnology, and Nanostructure Based Devices. Both basic and applied researches are presented. Among different results characterizing our knowledge about the nanoworld, including attempts to use it for information processing, one can note an increased interest to quantum dot systems. Depending on the size, composition and spatial distribution of quantum dots they can behave like artificial atoms, either independent or interacting in a specific lattice. Such systems exhibit indeed astonishing properties promising the birth of new generations of electronic, optoelectronic and optical devices.

The papers published in this book must be considered as preprinted notes, which will be enlightened at the Conference, in May 2001, where a detailed discussion of our understanding of the nanoworld is expected.

We deeply acknowledge Sponsors who provided financial support for the Conference.

Victor E. Borisenko
Francois Arnaud d'Avitaya
Co-chairmen of *NANOMEETING-2001*

Minsk and Marseille
January 2001

*14 December 1900, M. Planck presented to the German Physical Society his seminal paper putting forward radically new idea that the radiated energy can only be emitted in quanta. That day is considered to be the birth of quantum physics.

This page is intentionally left blank

CONTENTS

Foreword	vii
-----------------------	------------

PHYSICS OF NANOSTRUCTURES

Discovery and understanding of nanoworld in the XX-th century: main achievements in the mirror of the Nobel Prizes	3
---	----------

V. E. Borisenko

Self-assembled InGaAs quantum dot superlattices (invited)	15
--	-----------

M. Kawabe

Multiexciton dynamics of GaAs single quantum dots (invited)	22
--	-----------

K. Edamatsu, C. Watatani, T. Itoh, S. Shimomura, S. Hiyamizu

Photoreflectance Investigations of low dimensional semiconductor structures (invited)	30
--	-----------

J. Misiewicz, G. Sek, M. Bayer, A. Forchel

Thermoelectric properties of chaotic quantum dots (invited)	40
--	-----------

H. Buhmann, S. Maksimov, L. W. Molenkamp

Polarons in quantum wells (invited)	48
--	-----------

A. I. Bibik, M. O. Dzero, B. Gerlach, M. A. Smondyrev

Self-assembling SiGe dots: nucleation and growth (invited)	57
---	-----------

I. Berbezier, A. Portavoce, F. Volpi, A. Ronda

Stress and strain distributions in Ge dots on Si(001) by molecular dynamics simulation (invited)	69
---	-----------

P. Raiteri, F. Valentinotti, L. Miglio

Light emission from semiconducting silicide nanostructures in silicon (invited)	76
--	-----------

K. J. Kirkby, M. Lourenço, T. M. Butler, K. Homewood, C. N. Mckinty

Physics of multiwalled carbon nanotubes (invited)	86
<i>C. Schönenberger, L. Forró</i>	
Ultra thin C₆₀-based films: molecular arrangement and electronic states (invited).....	94
<i>C. Cepek, M. Sancrotti</i>	
On a possibility of the Mott transition in a quantum dot ensemble	102
<i>A. I. Bibik</i>	
Screening of extra point charge in a few particle coulomb system	106
<i>N. A. Poklonski, A. I. Siaglo, S. A. Vyrko, V. V. Mitianok</i>	
A superlattice with resonant states in a unit cell: the band structure and electron transitions	110
<i>A. V. Dmitriev, R. Keiper, V. V. Makeyev</i>	
Dispersion of guided plasmon-polaritons in a planar Bragg microresonator with two-dimensional electron system	114
<i>V. V. Popov, G. M. Thymalov</i>	
Optical properties of fractal Cantor-like multilayer nanostructures	118
<i>K. S. Sandomirski, S. V. Gaponenko, S. V. Zhukovsky, A. V. Lavrinenko</i>	
I-V curves of short intentionally disordered superlattices in vertical direction	122
<i>A. V. Dmitriev, O. V. Pupysheva, P. Thomas</i>	
Phonon-plasmon interaction in tunneling GaAs/AlAs superlattices: experiment and calculations	126
<i>M. D. Efremov, V. A. Volodin, V. A. Sachkov, V. V. Preobrazhenskii, B. R. Semyagin, E. A. Galaktionov</i>	
Negative and persistent positive photoconductivity in p-type Al_{0.5}Ga_{0.5}As/GaAs/Al_{0.5}Ga_{0.5}As	130
<i>E. V. Bogdanov, A. A. Ilievsky, N. Ya. Minina, A. M. Savin, O. P. Hansen, C. B. Sorensen, W. Kraak</i>	

Raman and photoluminescence studies of the interface reconstructions in GaAs/AlAs superlattices grown on (311) and (001) surfaces	134
<i>M. D. Efremov, V. A. Volodin, V. A. Sachkov, V. V. Preobrazhenskii, B. R. Semyagin, E. A. Galaktionov, A. V. Kretinin</i>	
Investigation of surface morphology features and local photoelectric properties of InAs/GaAs quantum dot structures.....	138
<i>V. Ya. Aleshkin, A. V. Biryukov, N. V. Vostokov, S. V. Gaponov, V. M. Danil'tsev, V. L. Mironov, A. V. Murel, O. I. Khrykin, V. I. Shashkin</i>	
Controllable one-dimensional photonic structures with <i>n-i-p-i</i> crystal layers	142
<i>V. N. Gusyatinikov, I. S. Nefedov, Yu. A. Morozov, V. K. Kononenko, D. V. Ushakov</i>	
Influence of electron irradiation on carrier recombination and intradot relaxation in InGaAs/GaAs quantum dot structures	146
<i>N. A. Sobolev, A. Cavaco, M. C. Carmo, H. Born, M. Grundmann, F. Heinrichsdorff, R. Heitz, A. Hoffmann, D. Bimberg</i>	
Electric field effect on absorption spectra of an ensemble of close-packed CdSe nanocrystals	150
<i>L. I. Gurinovich, M. V. Artemyev, U. Woggon</i>	
Ge nanocrystals in SiC: <i>ab initio</i> supercell calculations of optical properties	156
<i>H.-Ch. Weissker, J. Furthmüller, F. Bechstedt</i>	
Surface energies of Ge and Si and consequences for nanocrystallites	160
<i>A. A. Stekolnikov, J. Furthmüller, P. Käckell, F. Bechstedt</i>	
2D nanostructures and 3D silicide nanocrystallites at rare-earth metal/Si(111) interfaces: formation mechanism and properties	164
<i>T. V. Krachino, M. V. Kuz'min, M. V. Loginov, M. A. Mittsev</i>	

Photoluminescence of the silicon carbide nanoclusters embeded into porous silicon	168
<i>A. G. Rozhin, N. I. Klyui, V. G. Litovchenko, Yu. P. Piryatinskii, V. A. Makara, O. B. Korneta</i>	
Exciton recombination mechanism in light emitting nanocrystalline silicon	172
<i>A. V. Sachenko, E. B. Kaganovich, E. G. Manoilov</i>	
Time-resolved photoluminescence of nanocrystalline silicon films obtained by laser ablation	176
<i>E. B. Kaganovich, E. G. Manoilov, A. V. Sachenko, S. V. Svechnikov</i>	
Electron-phonon coupling in heavily doped silicon	180
<i>P. Kivinen, A. Savin, A. Manninen, J. Pekola, M. Prunnila, J. Ahopelto</i>	
Influence of surface phases on electrical conductivity of silicon surface.....	184
<i>D. A. Tsukanov, S. V. Ryzhkov, O. A. Utas, I. A. Belous, V. G. Lifshits</i>	
Morphology and optical properties of Si(111)/CrSi₂/Si and Si(111)/Mg₂Si/Si systems with self-organized quantum dots	190
<i>N. G. Galkin, A. M. Maslov, S. I. Kosikov, A. O. Talanov, K. N. Galkin</i>	
Microcavity enhancement of second-harmonic generation and Raman scattering in photonic crystals of porous silicon	194
<i>M. G. Martemyanov, T. V. Dolgova, A. I. MaYdikovskII, A. A. Fedyanin, O. A. Aktsipetrov, D. Schuhmacher, G. Marowsky, V. A. Yakovlev, G. Mattei</i>	
Structural and electrical characterization of thin crystalline CaF₂ layers grown by MBE on Si(111).....	198
<i>G. Guirléo, F. Bassani</i>	
Switching effect in lead phthalocyanine nanostructure	202
<i>N. A. Poklonski, E. F. Kislyakov, G. G. Fedoruk, D. I. Sagaidak, A. I. Siaglo, S. A. Vyrko</i>	

Photoreflectance diagnostics of nanometer dielectric films	206
<i>P. Adamson</i>	
Nanostructured $\text{TiO}_2\text{:Tb}_2\text{O}_3$ phosphor fabricated by sol-gel method on porous anodic alumina	210
<i>O. V. Sergeev, V. E. Borisenko, R. Heiderhoff, L. J. Balk</i>	
Three-dimensional photonic band gap structures doped with Tb^{3+} ions....	214
<i>N. V. Gaponenko, V. M. Shelekhina, O. A. Prokhorov, P. A. Vityaz, A. P. Stupak, A. N. Poryavina, S. V. Gaponenko, J. C. Pivin, A. V. Mudryi</i>	
Europium photoluminescence in sol-gel derived titania xerogel on porous anodic alumina	221
<i>I. S. Molchan, V. I. Pachinin, J. Misiewicz, R. Kudrawiec, G. E. Thompson, P. Skeldon, L. P. Mileszko</i>	
Dynamic observation and structure analysis of nanostructures of Cu on Si(111) by low energy electron microscopy	225
<i>T. Koshikawa, T. Yasue, M. Jalochoowski, E. Bauer</i>	
Optical properties of layer-periodic metal nanoparticle systems in the visible.....	235
<i>S. M. Kachan, A. N. Poryavina</i>	
Conductance quantization in magnetic and nonmagnetic metallic nanowires	239
<i>W. Nawrocki, M. Wawrzyniak</i>	
Conductivity of two-dimensional chromium and iron ordered surface phases on Si(111)	243
<i>N. G. Galkin, D. L. Goroshko, S. Ts. Krivoschapov</i>	
Effect of the symmetry on the properties of superconductor/normal metal nanostructures	247
<i>V. N. Kushnir, A. Yu. Petrov, S. L. Prischepa, A. Angrisani Armenio, C. Attanasio, L. Maritato</i>	

CHEMISTRY OF NANOSTRUCTURES

Self-assembling alkali nanowires at semiconductor surfaces (invited).....	255
<i>Maria Grazia Betti</i>	
Relaxation processes in self-assembled nanoscale photosynthetic models (invited)	263
<i>E. I. Zenkevich, A. M. Shulga, C. von Borczyskowski</i>	
Electronic processes in nanocomposite films (invited)	273
<i>R. D. Fedorovich, O. E. Kiyayev, A. G. Naumovets, P. M. Tomchuk</i>	
Size-control of small metal clusters and nanoparticles in zeolites: silver and copper in mordenites with variable $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio.....	281
<i>V. S. Gurin, N. E. Bogdanchikova, V. P. Petranovskii</i>	
Formation of ultradisperse bimetallic particles by redox processes in aqueous solutions	287
<i>Yu. A. Fedutik, Yu. V. Bokshits, G. P. Shevchenko</i>	
Polyelectrolyte micro- and nanocapsules as microcages for chemical reactions in restricted volumes	291
<i>G. B. Sukhorukov, I. L. Radtchenko, H. Möhwald</i>	
Employment of the layer-by-layer technique for the formation of polymer-core TiO_2-shell particles and TiO_2 hollow spheres	295
<i>A. S. Sussha, N. A. Shkorik, R. A. Caruso, F. Caruso</i>	
Observation of single molecule diffusion in micro- and nanodroplets of polymers on surfaces	299
<i>J. Schuster, F. Cichos, C. von Borczyskowski, J. Wrachtrup</i>	
Chemically grown II-VI semiconductor quantum dots for optoelectronic and photonic applications	304
<i>N. P. Gaponik, D. V. Talapin, S. K. Poznyak, A. S. Sussha, A. L. Rogach, A. Eychmüller</i>	

Fast electrochemical impedance spectroscopy for nanochemistry and nanophysics	308
--	------------

G. A. Ragoisha, A. S. Bondarenko

Kinetics of tip induced oxidation by scanning probe microscope	313
---	------------

S. A. Gavrilov, S. V. Lemesko, V. I. Shevyakov, V. M. Roschin

Features of luminescent semiconductor nanowire array formation by electrodeposition into porous alumina	317
--	------------

S. A. Gavrilov, D. A. Kravtchenko, A. I. Belogorokhov, E. A. Zhukov, L. I. Belogorokhova

Structural, electrical and gas sensing properties of copper phthalocyanine nanoparticles in polystyrene	321
--	------------

A. V. Misevich, A. E. Pochtenny, I. P. Ilyushonok, O. M. Stukalov

NANOTECHNOLOGY

Micro- and nanostructures: preparation and applications (invited)	329
--	------------

R. Kassing

Massively parallel atomic lines on silicon carbide (invited)	340
---	------------

P. Soukiasian

Formation of silicon and germanium nanostructures using ultrathin SiO₂ films (invited)	353
--	------------

M. Ichikawa

High temperature superconducting artificial superlattices: technology and perspectives (invited)	364
---	------------

L. Maritato

Semi-spherical SiGe/Si-nanostructures grown by MBE with <i>in situ</i> ion-beam assistance	372
---	------------

P. I. Gaiduk, J. Lundsgaard Hansen, A. Nylandsted Larsen

Molecular beam epitaxial growth and photoluminescence studies of InAs self-organized quantum dots on patterned GaAs (001) substrates	376
<i>B. C. Lee, H. M. Lee, J. C. Wu, Y. P. Chang, K. W. Sun, C. P. Lee</i>	
Production type planetary[®] MOVPE reactors for fabrication of nitride quantum well lasers	381
<i>B. Schineller, H. Protzmann, M. Luenenbuerger, M. Heuken, E. V. Lutsenko, G. P. Yablonskii</i>	
SPM modification of organic Langmuir-Blodgett films	386
<i>L. V. Kukhareenko, V. G. Leschenko, G. Y. Akulov, V. M. Anishchik, V. V. Grushevski, G. V. Krylova, A. I. Khmel'nitski</i>	
Advancing magnetic force microscopy	390
<i>I. Fedorov, V. Shevyakov, P. Prikhodko</i>	
Microporous xerogels in mesoporous anodic alumina	393
<i>N. V. Gaponenko</i>	
Technology of pillar microstructure formation with anodic oxides	399
<i>A. I. Vorobyova, E. A. Outkina</i>	
New materials and nanostructures for organic electroluminescent devices	403
<i>A. V. Kukhta, E. E. Kolesnik</i>	
Cadmium selenide nanocrystals inside plastic microspheres: a quantum dot in a photonic dot structure with unusual optical properties	408
<i>M. V. Artemyev</i>	
Porous silicon as a material for enhancement of electron field emission	412
<i>A. A. Evtukh, V. G. Litovchenko, Yu. M. Litvin, A. A. Efremov, Yu. V. Rassamakin, A. V. Sarikov, D. V. Fedin</i>	
On use of Bessel light beams in nanotechnologies	417
<i>N. S. Kazak, A. A. Ryzhevich, A. N. Khilo</i>	

Computer simulation of gas-phase plasma chemistry and silicon ion cluster formation during PECVD	424
---	------------

A. F. Stekolnikov, D. V. Feshchenko, T. A. Metelskiy, R. F. Belich

Development and application of nanostructured metallized fiber materials in microwave absorbers	428
--	------------

V. Bogush, V. Glybin, L. Lynkov

NANOSTRUCTURE BASED DEVICES

Carrier transport and electroluminescence in Si/CaF₂ superlattices (invited)	433
--	------------

V. Ioannou-Sougleridis, A. G. Nassiopoulou, T. Ouisse, F. Bassani, F. Arnaud d'Avitaya

Reverse biased porous silicon light emitting diodes for optoelectronics (invited)	441
--	------------

S. K. Lazarouk

Energy transfer and lasing in InGaN/GaN multiple quantum well heterostructures	450
---	------------

G. P. Yablonskii, A. V. Mudryi, E. V. Lutsenko, V. N. Pavlovskii, I. P. Marko, V. Z. Zubialevich, B. Schineller, H. Protzmann, M. Luenenbuerger, M. Heuken

A new multipeak resonant tunneling diode for signal processing application	454
---	------------

A. N. Kholod, M. Liniger, A. Zaslavsky, A. L. Danilyuk, F. Arnaud d'Avitaya

A cyclotron resonance quantum Hall effect detector	459
---	------------

B. A. Andreev, I. V. Erofeeva, V. I. Gavrilenko, A. L. Korotkov, A. N. Yablonskiy, O. Astafiev, Y. Kawano, R. S. Komiyama

The role of shallow and deep traps in carrier transport across silicon/insulator nanostructures	463
--	------------

J. A. Berashevich, A. L. Danilyuk

Long term charge relaxation in silicon single electron transistors	466
<i>A. Savin, A. Manninen, P. Kivinen, J. Pekola, M. Prunnila, J. Ahopelto, M. Kamp, M. Emmerling, A. Forchel</i>	
Intersubband electron scattering rates in one-dimensional Si MOS-structure	470
<i>V. M. Borzdov, V. O. Galenchik, O. G. Zhevnyak, F. F. Komarov</i>	
The potential of β-FeSi₂ nanostructures for solar cell applications	473
<i>C. N. Mckinty, K. J. Kirkby, K. P. Homewood, S.-P. Edwards, G. Shao, R. Valizadeh, J. S. Colligon</i>	
Resonant tunneling through an array of quantum dots coupled to superconductors under the effect of magnetic field	476
<i>A. N. Mina</i>	
Modeling of the differential conductance of mesoscopic system: theory and simulation	480
<i>A. H. Aly</i>	
Author index	485

PHYSICS OF NANOSTRUCTURES

This page is intentionally left blank

DISCOVERY AND UNDERSTANDING OF NANOWORLD IN THE XX-th CENTURY: MAIN ACHIEVEMENTS IN THE MIRROR OF THE NOBEL PRIZES

V. E. BORISENKO

*Belarusian State University of Informatics and Radioelectronics
P. Browka 6, 220013 Minsk, Belarus*

E-mail: borisenko@nano.bsuir.edu.by

A historical survey of main contributions made possible to understand phenomena in nanoworld, which is the world spreading from individual atoms to low-dimensional structures, is composed on the basis of the achievements awarded the Nobel Prizes.

The XX-th century has written the most impressive pages in the book of understanding of nature. That century was illuminated by discoveries and studies of quantum phenomena that were completely unknown. Revolutionary new ideas on the theoretical basis of quantum physics were formulated, thus providing development of novel technologies, tools and devices. They have covered not only physics, but also chemistry, biology, medicine and their related applied areas.

Electrons and light have been recognized to behave as particles and waves simultaneously. It is indeed pronounced in systems having at least one dimension in the nanometre ($1 \text{ nm} = 10^{-9} \text{ m}$) range. The term "nanoworld" appeared in the end of the XX-th century in order to represent such systems and particular phenomena there. In fact, the nanoworld spreads from individual atoms and molecules to their ensembles and low-dimensional structures which behavior is regulated by quantum-wave nature of electrons and photons. Nanoworld is considered to have the greatest potential for a progress in information technologies in the XXI-st century.

Main contributors and their discoveries providing understanding of nanoworld [1-6] are listed below in the chronological order they were recognized by the Nobel Foundation. The Nobel Prize institution has been chosen as a mirror for that, as far as the prizes cover many of the outstanding contributions to physics and chemistry, while a complete historical survey would definitely need an extension of the list of names and phenomena.

1902 (physics): Hendrik Antoon Lorentz (Leiden University, The Netherlands) and **Pieter Zeeman** (Amsterdam University, The Netherlands) - in recognition of the extraordinary service they rendered by their researches into the influence of magnetism upon radiation phenomena.

The mechanisms of light emission by carriers of electric charge was studied by H. A. Lorentz, who was one of the first to apply Maxwell's equations to electric

charges in matter. His theory could also be applied to the radiation caused by vibrations in atoms.

As early as 1896, P. Zeeman, who was looking for possible effects of electric and magnetic fields on light, made an important discovery, namely, that spectral lines from sodium in a flame were split up into several components when a strong magnetic field was applied.

1906 (physics): Sir Joseph John Thomson (Cambridge University, GB) - in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases.

In 1897, J. J. Thomson, who worked with rays emanating from the cathode in partly evacuated discharge tubes, identified the carriers of electric charge [7]. He showed that these rays consisted of discrete particles, later called "electrons". He measured a value for the ratio between their mass and (negative) charge, and found that it was only a very small fraction of that expected for singly charged atoms. It was soon realized that these lightweight particles must be the building blocks that, together with the positively charged nuclei, make up all different kinds of atoms.

1913 (physics): Heike Kamerlingh-Onnes (Leiden University, The Netherlands) - for his investigations on the properties of matter at low temperatures which led, inter alia, to the production of liquid helium.

In 1911, H. Kamerlingh-Onnes discovered superconductivity. He noticed that the electrical resistivity of mercury dropped to less than one billionth of its ordinary value when it was cooled well below a transition temperature, which is about 4 K [8].

1918 (physics): Max Karl Ernst Ludwig Planck (Berlin University, Germany) - in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta.

In December 1900, M. Planck presented to the German Physical Society his seminal paper putting forward radically new idea that the radiated energy can only be emitted in quanta, *i.e.* portions that have a certain definite value, larger for the short wavelengths than for the long ones (equal to a constant times the frequency for each quantum) [9]. December 1900 is considered to be the birth of quantum physics.

1919 (physics): Johannes Stark (Greifswald University, Germany) - for his discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields.

In 1907, J. Stark demonstrated the direct effect of electric fields on the emission of light, by exposing beams of atoms ("anodic rays", consisting of atoms or molecules) to strong electric fields [10]. He observed a complicated splitting of spectral lines as well as a Doppler shift depending on the velocities of the emitters.

1921 (physics): Albert Einstein (Kaiser-Wilhelm-Institut für Physik, now Max-Planck-Institute, Berlin-Dahlem, Germany) - for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect.

In 1904-1905, A. Einstein interpreted the photoelectric effect (first observed in 1887 by Hertz) and extended Planck's theory of black-body radiation in terms of energy quanta [11]. In 1905 he presented his special theory of relativity, which expressed the mass-energy relationship. He also made important contributions to the quantum theory of the specific heats of solids (1907) and to energy fluctuations (1909).

1922 (physics): Niels Henrik David Bohr (Copenhagen University, Denmark) - for his services in the investigation of the structure of atoms and of the radiation emanating from them.

In 1913, N. Bohr worked out a planetary picture of electrons circulating around the nucleus of an atom [12]. Later (1914-1915) he found that the sharp spectral lines emitted by the atoms could only be explained if the electrons were circulating in stationary orbits characterized by a quantized angular momentum and that the emitted frequencies corresponded to emission of radiation with energy equal to the difference between quantized energy states of the electrons [13].

1923 (physics): Robert Andrews Millikan (California Institute of Technology, Pasadena, USA) - for his work on the elementary charge of electricity and on the photoelectric effect.

In 1912, R. A. Millikan made the first precision measurements of the electron charge with the oil-drop method [14] and contributed to the quantum description of the photoelectric effect [15].

1929 (physics): Prince Louis-Victor Pierre Raymond de Broglie (Sorbonne University, Institut Henri Poincaré, Paris, France) - for his discovery of the wave nature of electrons.

In 1923, L. de Broglie proposed that material particles may also show wave properties, now that electromagnetic radiation had been shown to display particle aspects in the form of photons [16]. He developed mathematical expressions for this dualistic behavior, including what has later been called the "de Broglie wavelength" of a moving particle.

1930 (physics): Sir Chandrasekhara Venkata Raman (Calcutta University, India) - for his work on the scattering of light and for the discovery of the effect named after him.

In 1928, C. V. Raman discovered that light scattered from molecules contained components which were shifted in frequency with respect to the infalling monochromatic light [17]. These shifts are caused by the molecules' gain or loss of characteristic amounts of energy when they change their rotational or vibrational motion. The effect was also independently observed by Russian scientists G. Landsberg and L. Mandelstam in St. Petersburg [18]. Raman spectroscopy soon became an important source of information on molecular structure and dynamics.

1932 (physics): Werner Karl Heisenberg (Leipzig University, Germany) - for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen.

In the late 1920s, W. K. Heisenberg developed a mathematically different approach in quantum mechanics, called "matrix mechanics". He arrived to the conclusion that there are natural limitations on the accuracy by which certain quantities can be measured simultaneously (Heisenberg's uncertainty relations) [19].

1932 (chemistry): Irving Langmuir (General Electric Company, Schenectady, USA) - for his discoveries and investigations in surface chemistry.

In 1916-1918, I. Langmuir discovered importance of chemical events at an interface of two phases (for example, solid and liquid) [20] and showed that phenomena at such interfaces have important applications all the way from technical to physiological processes. He was the first industrial scientist to receive the Nobel Prize.

1933 (physics): Erwin Schrödinger (Berlin University, Germany) and **Paul Adrien Maurice Dirac** (Cambridge University, GB) - for the discovery of new productive forms of atomic theory.

In 1926, E. Schrödinger further developed wave ideas of de Broglie in quantum mechanics and created what has been called "wave mechanics" [21]. In 1925-1926, P. A. M. Dirac constructed a modified formalism which took into account effects of Einstein's special relativity [22], and showed that such a theory not only contained terms corresponding to the intrinsic spinning of electrons (and therefore explaining their own intrinsic magnetic moment and the fine structure observed in atomic spectra), but also predicted the existence of a completely new kind of particles, the so-called antiparticles with identical masses but opposite charge. The first antiparticle to be discovered, that of the electron, was observed in 1932 by C. D. Anderson and was given the name "positron" (one half of the Physics Prize for 1936).

1936 (chemistry): Petrus Josephus Wilhelmus Debye (Berlin University, Germany) - for his contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases.

In 1916-1923, P. Debye employed electron diffraction and the measurement of dipole moments to get structural information [23]. Dipole moments are found in molecules, in which the positive and negative charge is unevenly distributed (polar molecules).

1937 (physics): Clinton Joseph Davisson (Bell Telephone Laboratories, New York, USA) and **George Paget Thomson** (London University, GB) - for their experimental discovery of the diffraction of electrons by crystals.

In 1923, C. J. Davisson and C. H. Kunsman indicated that electrons could actually show reflection effects similar to that of waves hitting a crystal [24] and these experiments were now repeated, verifying the associated wavelength predicted by de Broglie. Somewhat later (1927), G. P. Thomson (son of J. J. Thomson) and A. Reid made much improved experiments on higher energy electrons penetrating thin metal foils, which showed very clear diffraction effects [25].

1938 (physics): Enrico Fermi (Rome University, Italy) - for his demonstrations of the existence of new radioactive elements produced by neutron irradiation, and for his related discovery of nuclear reactions brought about by slow neutrons.

Among the outstanding contributions of E. Fermi to physics, his quantum statistics of electrons in matter developed in 1926 [26] is one of the most important discovery for modern understanding of nanoworld.

1945 (physics): Wolfgang Pauli (Princeton University, USA) - for the discovery of the Exclusion Principle, also called the Pauli Principle.

In 1925, W. Pauli formulated his exclusion principle, which states that "there can never exist two or more equivalent electrons in the atom for which the values of all quantum numbers coincide" [27].

1954 (physics): Max Born (Edinburgh University, GB) - for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wavefunction.

In the 1920s, M. Born contributed to mathematical formulation and physical interpretation of quantum mechanics [28].

1954 (chemistry): Linus Carl Pauling (California Institute of Technology, Pasadena, USA) - for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances.

In the 1930s, L. C. Pauling developed the concept of valence bonds providing the background for quantum chemistry [29]. He is the only person to date to have won two unshared Nobel Prizes. The second one is the Nobel Peace Prize for 1962.

1955 (physics): Willis Eugene Lamb (Stanford University, USA) - for his discoveries concerning the fine structure of the hydrogen spectrum and **Polykarp Kusch** (Columbia University, New York, USA) - for his precision determination of the magnetic moment of the electron.

In 1947, W. E. Lamb found that the fine structure splitting of optical radiation from hydrogen did not have exactly the Dirac value and differed from it [30]. That stimulated a reconsideration of the basic concepts behind the application of quantum theory to electromagnetism. In 1947, P. Kusch measured precisely the magnetic moment of an electron [31] and showed that it did not have exactly the value predicted by Dirac, but differed from it by a small amount.

1956 (physics): William Bradford Shockley (Semiconductor Laboratory of Beckman Instruments Inc., Mountain View, USA), **John Bardeen** (University of Illinois, Urbana, USA) and **Walter Houser Brattain** (Bell Telephone Laboratories Murray Hill, USA) - for their researches on semiconductors and their discovery of the transistor effect.

In 1947-1949, W. Shockley, J. Bardeen and W. H. Brattain working in the Bell Telephone Laboratories carried out fundamental investigations of semiconductors and developed the first transistor [32]. This was the beginning of the era of solid state electronics.

1962 (physics): Lev Davidovich Landau (Academy of Sciences, Moscow, USSR) - for his pioneering theories for condensed matter.

L. D. Landau proposed the concept of quantum liquids in condensed matter. The theory of Bose type liquids (1941-1947) and then Fermi type liquids (1956-1958) [33] was formulated, providing an understanding of an electron behavior in solids.

1964 (physics): Charles Hard Townes (Massachusetts Institute of Technology, Cambridge, USA), **Nicolay Gennadiyevich Basov** (Lebedev Institute for Physics, Academy of Sciences, Moscow, USSR) and **Aleksandr Mikhailovich Prokhorov** (Lebedev Institute for Physics, Academy of Sciences, Moscow, USSR) - for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle.

In 1958, A. L. Schawlow and C. H. Townes created the first maser used a stimulated transition in the ammonia molecule [34]. It emitted an intense microwave radiation, which unlike that of natural emitters, was coherent, *i.e.* with all photons in phase. (A. L. Schawlow received the Nobel Prize in 1981 for his contribution to the development of laser spectroscopy). Theoretical principles of masers and lasers were developed by N. G. Basov and A. M. Prokhorov in 1958-1960 [35].

1966 (physics): Alfred Kastler (École Normale Supérieure, Université de Paris France) - for the discovery and development of optical methods for studying Hertzian resonances in atoms.

In the 1950s, A. Kastler and his co-workers showed that electrons in atoms can be put into selected excited substates by the use of polarized light [36]. After radiative decay, this can also lead to an orientation of the spins of ground-state atoms. The subsequent induction of radio frequency transitions opened possibilities to measure properties of the quantized states of electrons in atoms in much greater detail than before.

1966 (chemistry): Robert S. Mulliken (University of Chicago, USA) - for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method.

In 1927-1928, R. S. Mulliken developed the theory of molecular orbitals considering in quantum-mechanical terms the interaction between all atomic nuclei and electrons in a molecule [37].

1970 (physics): Louis Eugène Félix Néel (University of Grenoble, France) - for fundamental work and discoveries concerning antiferromagnetism and ferrimagnetism which have led to important applications in solid state physics.

In 1932, L. Néel discovered antiferromagnetism that is a form of magnetism in which the magnetic moment or „spins“ on neighboring atoms point in opposite directions and cancel each other [38]. Previously only three forms of magnetism – diamagnetism, paramagnetism and ferromagnetism – were known. He showed that an antiferromagnetic state disappears above a certain temperature, which is now

known as the Néel point. Moreover, the strong magnetism observed in ferrite materials was also explained by him [39]. He proposed that a similar system of opposing spins exists in these materials, but that an imbalance between the spins results in a permanent external magnetic field. That phenomenon was labelled by him ferrimagnetism.

1972 (physics): John Bardeen (University of Illinois, Urbana, USA), **Leon Neil Cooper** (Brown University, Providence, USA) and **John Robert Schrieffer** (University of Pennsylvania, Philadelphia, USA) - for their jointly developed theory of superconductivity, usually called the BCS-theory.

In 1956-1957, J. Bardeen, L. N. Cooper and J. R. Schrieffer formulated a theory based on the idea that pairs of electrons with opposite spins and directions of motion can lower their energy by an amount by sharing exactly the same deformation of the crystalline lattice as they move [40]. Such "Cooper pairs" act as bosonic particles. This allows them to move as a coherent macroscopic fluid, undisturbed as long as the thermal excitations are lower in energy than the energy gained by the pair formation.

1973 (physics): Leo Esaki (IBM Thomas J. Watson Research Center, Yorktown Heights, USA), **Ivar Giaever** (General Electric Company, Schenectady, USA) - for their experimental discoveries regarding tunneling phenomena in semiconductors and superconductors, respectively, and **Brian David Josephson** (Cambridge University, GB) - for his theoretical predictions of the properties of a supercurrent through a tunnel barrier, in particular those phenomena which are generally known as the Josephson effects.

In 1958, L. Esaki discovered tunneling phenomena in semiconductors and developed the tunnel diode [41], an electronic component that has a negative differential resistance, a technically interesting property. In 1960, I. Giaever invented and studied the detailed properties of tunnel junctions formed by superconductors [42]. In 1962, B. D. Josephson analyzed the transfer of superconducting carriers between two superconducting metals, separated by a very thin layer of normal-conducting material. He found that the quantum phase, which determines the transport properties, is an oscillating function of the voltage applied over this kind of junction [43].

1977 (physics): Philip Warren Anderson (Bell Telephone Laboratories, Murray Hill, USA), **Sir Nevill Francis Mott** (Cambridge University, Cambridge, GB) and **John Hasbrouck van Vleck** (Harvard University, Cambridge, USA) - for their fundamental theoretical investigations of the electronic structure of magnetic and disordered systems.

In the end of the 1950s, P. W. Anderson made several important contributions to the theory of electronic structures in metallic systems, in particular concerning the effects of inhomogeneities in alloys and magnetic impurity atoms in metals [44]. In the 1940s-1950s, N. F. Mott studied general conditions for electron conductivity in solids and formulated rules for the point at which an insulator becomes a conductor (the Mott transition) when composition or external parameters are

changed [45]. In the 1930s, J. H. van Vleck made significant contributions to the theory of magnetism in condensed matter in the years following the creation of quantum mechanics [46]. He calculated the effects of chemical binding on the paramagnetic atoms and explained the effects of temperature and applied magnetic fields on their magnetism. In particular, he developed the theory of crystal field effects on the magnetism of transition metal compounds, which has been of great importance for understanding the function of active centers in compounds for laser physics as well as in biomolecules.

1985 (physics): Klaus von Klitzing (Max-Planck-Institute for Solid State Research, Stuttgart, Germany) - for the discovery of the quantized Hall effect.

In 1980, K. von Klitzing with co-authors discovered the quantized Hall effect [47]. When a strong magnetic field is applied perpendicular to the plane of a quasi two-dimensional layer, the quantum conditions are such that an increase of magnetic field does not give rise to a linear increase of voltage on the edges of the sample, but a step-wise one. Between these steps, the Hall resistance is quantized, providing a possibility to measure the ratio between two fundamental constants, *i.e.* electron charge and Planck's constant, very exactly. It has important consequences for measurement technology.

1986 (physics): Ernst Ruska (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany) - for his fundamental work in electron optics and for the design of the first electron microscope, **Gerd Binnig** and **Heinrich Rohrer** (both IBM Zurich Research Laboratory, Rüschlikon, Switzerland) - for their design of the scanning tunneling microscope.

Early in the 1930s, E. Ruska made fundamental studies in electron optics and designed the first working electron microscope [48]. In 1982, G. Binnig and H. Rohrer developed a completely different way to obtain pictures with extremely high resolution [49]. Their method is applicable to surfaces of solids and is based on the tunneling of electrons from very thin metallic tips to atoms on the surface when the tip is moved at very close distance to it (about 1 nm). By keeping the tunneling current constant a moving tip can be made to follow the topography of the surface, and pictures are obtained by scanning over the area of interest. By this method, single atoms on surfaces can be visualized.

1987 (physics): J. Georg Bednorz and **K. Alexander Müller** (both IBM Research Laboratory, Rüschlikon, Switzerland) - for their important break-through in the discovery of superconductivity in ceramic materials.

In 1986, J. G. Bednorz and K. A. Müller showed that a lanthanum-copper oxide (La_2CuO_4) could be made superconducting up to 35 K by doping it with small amounts of barium [50]. Soon thereafter, other laboratories reported that cuprates of similar structure were superconducting up to about 100 K. This discovery of "high temperature superconductors" triggered one of the greatest efforts in modern physics: to understand the basic mechanism for superconductivity in these extraordinary materials.

1996 (chemistry): Robert F. Curl Jr. (Rice University, Houston, USA), **Sir Harold W. Kroto** (University of Sussex, Brighton, GB) and **Richard E. Smalley** (Rice University, Houston, USA) - for their discovery of fullerenes.

In 1985 H. W. Kroto, R. F. Curl, R. E. Smalley and J. R. Heath discovered compounds, called fullerenes, in which 60 or 70 carbon atoms are bound together in clusters in the form of a ball [51]. The designation fullerenes is taken from the name of an American architect, R. Buckminster Fuller, who had designed a dome having the form of a football for 1967 Montreal World Exhibition.

1998 (physics): Robert B. Laughlin (Stanford University, Stanford, USA), **Horst L. Störmer** (Columbia University, New York, USA) and **Daniel C. Tsui** (Princeton University, Princeton, USA) - for their discovery of a new form of quantum fluid with fractionally charged excitations.

In 1982 D. C. Tsui, H. L. Störmer and A. C. Gossard presented results of refined studies of the quantum Hall effect using inversion layers in materials of ultra-high purity [52]. Plateaus appeared in the Hall effect not only for magnetic fields corresponding to the filling of orbits with one, two, three, etc, electron charges, but also for fields corresponding to fractional charges! This could be understood only in terms of a new kind of quantum fluid, where the motion of independent electrons is replaced by excitations in a multi-particle system which behave as fractionally charged ones. In 1983 R. B. Laughlin developed the theory that describes this new form of quantum fluid with fractionally charged excitations [53].

1998 (chemistry): Walter Kohn (University of California, Santa Barbara, USA) - for his development of the density-functional theory and **John A. Pople** (Northwestern University, Evanston, USA) - for his development of computational methods in quantum chemistry.

In 1964-1965, W. Kohn developed the density functional theory [54], which is applicable to free atoms as well as to electrons in molecules and solids. He developed methods of treating quantum exchange correlations, by which important limitations for the predictive power of electronic structure calculations, in solids as well as molecules, have been overcome. In the 1950s-1960s, J. A. Pople with co-workers designed computer programs based on classical quantum theory as well as on density-functional theory [55].

2000 (physics): Zhores I. Alferov (A. F. Ioffe Physico-Technical Institute, St. Petersburg, Russia) and **Herbert Kroemer** (University of California, Santa Barbara, USA) - for developing semiconductor heterostructures used in high-speed- and opto-electronics and **Jack S. Kilby** (Texas Instruments, Dallas, USA) - for his part in the invention of the integrated circuit.

In the 1960s, Zh. I. Alferov with co-workers and H. Kroemer independently invented and developed fast opto- and microelectronic components based on layered semiconductor structures, termed semiconductor heterostructures [56,57]. Their outstanding contributions to physics and technology of III-V semiconductor heterostructures, especially investigations of injection properties, development of

lasers, solar cells, LED's, and epitaxy processes have led to the creation of modern heterostructure physics and electronics.

In the end of the 1950s, J. S. Kilby proposed and first realized the concept of integration of electronic components within a semiconductor chip [58]. He invented and developed a series of integrated circuits covered by his over 60 US patents. Through this invention microelectronics became the basis of the information technologies in the XX-th century.

In conclusion, it is clear that nanoworld and its fundamental understanding originated from the marriage of electron and photon in which they demonstrated both particle and wave nature. The mirror of the Nobel Prizes has less than 100 % reflectivity in nanoworld. There are some discoveries left, like single-electron tunneling, interference and spin effects in carrier transport, quantized conductance, theory and practice of quantum computations, molecular electronics, which could be recognized at the level of the Nobel Prizes.

References

1. *Twentieth Century Physics*, Vols. I, II, III, ed. by L. M. Brown, A. Pais, B. Pippard (AIP Press, New York, 1995).
2. *Nobel e-museum* (<http://www.nobel.se>).
3. Karlsson E. B., The Nobel Prize in Physics 1901-1999, *Nobel e-museum*, February 2000.
4. Malmström Bo G., The Nobel Prize in chemistry: the development of modern chemistry, *Nobel e-museum*, December 1999.
5. *Nobel lectures in Physics (1901-1995)* (World Scientific, Singapore 2000).
6. *Nobel lectures in Chemistry (1901-1995)* (World Scientific, Singapore 2000).

Pioneering publications of the Nobel Laureates

7. Thomson J. J., *Phil. Mag.* **44** (1987) 293; **48** (1987) 547.
8. Kamerling-Onnes H., *Leiden Comm.* 120b, 122b, 124c (1911).
9. Plank M., *Verh. Deutsch. Phys. Ges.* **2** (1900) 237.
10. Stark J., *Phys. Z.* **8** (1907) 913.
11. Einstein A., *Ann. Phys. Lpz.* **14** (1904) 354; **17** (1905) 132.
12. Bohr N., *Phil. Mag.* **26** (1913) 1, 476, 857.
13. Bohr N., *Phil. Mag.* **30** (1915) 394.
14. Millikan R. A., *Phys. Rev.* **4** (1914) 73; **6** (1915) 55; **7** (1916) 362.
15. Millikan R. A., *Phys. Rev.* **7** (1916) 355.
16. de Broglie L., *C. R. Acad. Sci. (Paris)* **177** (1923) 507.
17. Raman C. V., *Indian J. Phys.* **2** (1928) 387.
18. Landsberg G., Mandelstam L., *Z. Phys.* **50** (1928) 769.
19. Heisenberg W., *Z. Phys.* **43** (1927) 172.
20. Langmuir I., *J. Am. Chem. Soc.* **38** (1916) 2221; **40** (1918) 1361.

21. Schrödinger E., *Phys. Z.* **27** (1926) 95; *Ann. Phys., Lpz.* **79** (1926) 361, 489, 734; *Ann. Phys., Lpz.* **81** (1926) 109.
22. Dirac P. A. M., *Proc. Royal Soc.* **A109** (1925) 642; **A110** (1926) 561; **111** (1926) 281, 405.
23. Debye P., *Nach. Ges. Wiss. (Göttingen)* (1916) 142; *Phys. Z.* **24** (1923) 161.
24. Davisson C. J., Kunsman C. H., *Phys. Rev.* **22** (1923) 242.
25. Thomson G. P., Reid A., *Nature* **119** (1927) 890.
26. Fermi E., *Z. Phys.* **36** (1926) 902.
27. Pauli W., *Z. Phys.* **31** (1925) 765.
28. Born M., *Z. Phys.* **26** (1924) 379.
29. Pauling L., *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1939).
30. Lamb W. E., Reserford R. C., *Phys. Rev.* **72** (1947) 241.
31. Kusch P., Foley H. M., *Phys. Rev.*, **72** (1947) 1256; **73** (1948) 412; **74** (1948) 250.
32. Bardeen J., Brattain W. H., *Phys. Rev.* **74** (1948) 230; Bardeen J., Brattain W. H., *US Patent* n°2524035 (1948); Shockley W., *Bell Syst. Tech. J.* **28** (1949) 435.
33. Landau L. D., *Sov. Phys.-JETP* **3** (1957) 920.
34. Schawlow A. L., Townes C. H., *Phys. Rev.*, **112** (1958) 1940; *US Patent* n°2929922 (1960).
35. Prokhorov A. M., *Sov. Phys.-JETP* **7** (1958) 1140; Basov N. G., Vul B. M., Popov Y. M., *Sov. Phys.-JEPT* **10** (1960) 416.
36. Brossel J., Kastler A., *C. R. Acad. Sci. (Paris)* **229** (1949) 1213; Kastler A., *J. Phys.* **11** (1950) 255.
37. Mulliken R. S., Leipziger Universittswoche – Quantentheorie und Chemie (Leipzig, 1928).
38. Néel L., *Ann.Phys. (Paris)* **17** (1932) 5; **5** (1936) 232.
39. Néel L., *Ann.Phys. (Paris)* **3** (1948) 137.
40. Cooper L. N., *Phys. Rev.* **104** (1956) 1189; Bardeen J., Cooper L. N., Schrieffer J. R., *Phys. Rev.* **108** (1957) 1175.
41. Esaki L., *Phys. Rev.* **109** (1958) 603.
42. Giaever I., *Phys. Rev. Lett.* **5** (1960) 147, 464.
43. Josephson B. D., *Phys. Lett.* **1** (1962) 251.
44. Anderson P. W., *Phys. Rev.* **109** (1958) 1492.
45. Mott N. F., Jones N. F., *Theory of the Properties of Metals and Alloys* (Clarendon, Oxford, 1936); Mott N. F., Nabarro F. R. N., *Proc. Phys. Soc.* **52** (1940) 86; Mott N. F., *Can. J. Phys.* **34** (1956) 1356.
46. van Vleck J. H., *Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932).
47. von Klitzing K., Dorda G., Pepper M., *Phys. Rev. Lett.* **45** (1980) 494.
48. Ruska E., *The Early Development of Electron Lenses and Electron Microscopy* (Hirzel, Stuttgart, 1980).

49. Binning G., Rohrer H., *Helv. Phys. Acta* **55** (1982) 726.
50. Bednorz J. G., Müller K. A., *Z. Phys. B* **64** (1986) 189.
51. Kroto H. W., Curl R. F., Smalley R. E., Heath J. R., *Nature* **318** (1985) 162.
52. Tsui D. C., Störmer H. L., Gossard A. C., *Phys. Rev. Lett.* **48** (1982) 1559.
53. Laughlin R. B., *Phys. Rev. Lett.* **50** (1983) 1395.
54. Hohenberg P., Kohn W., *Phys. Rev.* **136** (1964) 864; Kohn W., Sham L. J., *Phys. Rev.* **140** (1965) 1133.
55. Pople J. A., Nesbet R. K., *J. Chem. Phys.* **22** (1954) 571; Hehre W. J., Stewart R. F., Pople J. A., *J. Chem. Phys.* **51** (1969) 2657; Hehre D. J., Lathan W. A., Newton M. D., Ditchfield R., Pople J. A., *GAUSSIAN-70, Program number 236, QCPE* (Indiana University, Bloomington, Indiana, 1970).
56. Alferov Zh. I., Kazarinov R. F., *Inventor's Certificate* n°181737 (1963); Alferov Zh. I., *Fiz. Tekhn. Poluprovodn.* **1** (1967) 436 (in Russian); Alferov Zh. I., Andreev V. M., Garbuzov D. Z., Zilyaev Y. V., Morozov E. P., Portnoi E. L., Trofim V. G., *Sov. Phys. Semicond.* **4** (1971) 1553.
57. Kroemer H., *RCA Rev.* **18** (1957) 332; *Proc. IEEE* **51** (1963) 1782.
58. Kilby J. S., *Electronics* **32** (1959) 110; *IEEE Trans. Electron. Dev.* **23** (1976) 648.

INVITED

SELF-ASSEMBLED InGaAs QUANTUM DOT SUPERLATTICES

M. KAWABE

*Institute of Applied Physics, University of Tsukuba
Tsukuba, Ibaraki, 305-8573, Japan*

E-mail: kawabe@ims.tsukuba.ac.jp

Well-ordered high-density quantum dot arrays of InGaAs have been fabricated on high-index substrates by atomic-hydrogen assisted molecular beam epitaxy. The density and the dot size are controlled by growth temperature and substrate structure. The dot growth mechanism is explained not only by simple strain relaxation but also by phase separation. The surface coverage of the high density quantum dots is almost 100 %, which implies the lateral coupling between the dots. Photoluminescence and photoconductivity measurements show the existence of minibands formed by lateral coupling of dots.

1 Introduction

Development of a technology for high-density integration of quantum dots (QDs) is one of the important objectives for high-efficiency optical devices, single electron devices and low-dimensional physics. Self-organization of QDs is a promising method for high-density QD formation. A number of systems with a large lattice mismatch have been studied. Under the suitable conditions the deposited materials form elastically strained, defect-free three-dimensional islands. Control of size can be achieved by optimizing the growth conditions such as growth rate, growth temperature and film thickness. However, controlling the density and the ordering of QDs is a crucial issue to be resolved. Moreover, the control of coupling between QDs is also very important for further development of low-dimensional devices and low-dimensional physics. Electronic coupling between QDs has been utilized by stacking QD layers vertically [1,2]. Up to now, ordering and coupling of QDs have received intensive studies which aim at the realization of quantum dot superlattices [3-8].

In this paper, we report on the realization of high-density InGaAs QD arrays which are laterally coupled. There is a control of coupling strength in the case of GaAs(311)B substrates. In addition to a description of detailed growth conditions, a growth mechanism which is different from the usual Stranski-Krastanov(S-K) mode is also investigated. Not only the appearance of QD arrays, the electronic state of them was studied by photoluminescence and photoconductivity. It has been confirmed by time resolved photoluminescence and photoluminescence excitation spectrum that the extended states are formed in these QD arrays. Electrical

conduction shows negative differential resistance which is also explained by the existence of extended states.

2 High density quantum dots

In our previous work we have shown that well-ordered InGaAs QDs were fabricated on GaAs(311)B substrates by using atomic hydrogen-assisted molecular beam epitaxy (H-MBE) where atomic hydrogen was supplied on growing surface [9]. It is well known that atomic hydrogen removes surface contamination on substrate at low temperature [10]. The critical thickness for lattice relaxation in highly mismatched system was increased and the surface morphology was improved by atomic hydrogen as well [11].

The growth chamber is equipped with a hydrogen cracker in which hydrogen molecules are cracked by a hot tungsten filament. The atomic hydrogen flux which is approximately 1×10^{16} at/cm²s in this experiment, can be controlled by the flow rate of hydrogen molecule and the filament temperature. GaAs(311)B substrates were cleaned with atomic hydrogen at 500 °C. After deposition of GaAs buffer layers InGaAs QDs were grown at various temperatures ranging from 460 °C to 540 °C with the rate of 0.1 μm/h. Reflection high-energy electron diffraction (RHEED) was used to monitor the surface reconstruction, morphology and lateral lattice constant of the surface during growth. Surface morphology, as well as the size and position of the QDs, was studied by an atomic force microscope (AFM) in air. Photoluminescence (PL) and time resolved photoluminescence measurements were carried out at 4.2 K and 5 K by using Ar ion laser and Ti:sapphire laser. The sample for PL had GaAs a cap layer of about 15 nm on QDs. For the in-plane transport measurement, a slightly modified structure which had in-plane electrode on the doped cap layer was used and the transport properties were measured by photocurrent.

Fig. 1(a-d) shows the dependence of size and density of QDs on the growth temperature. The fast Fourier transforms are shown for reference. It is found that the QD diameter decreases from 120 nm at 520 °C to 20 nm at 460 °C, while the density increases from 5.6×10^9 cm⁻² to 1.4×10^{11} cm⁻², accompanying deterioration of ordering. With decreasing growth temperature, the QDs became highly-packed and particularly in (c) and (d) the surface coverage of QDs was almost 100 %. Ordering of QDs is explained by repulsive forces which originate from induced strain in substrates [12,13]. In the S-K mode, when the thickness increases over a critical value, two dots generally merge into one large dot and the strain energy is relaxed as dislocations are incorporated in the dot [14]. However, as shown in Fig. 1(d), QDs do not merge to form larger QDs beyond the thickness where all the QDs are in contact and the surface coverage becomes 100 %. A plan view of TEM image for the high density QDs (not shown) indicates that the boundary of the nearest two dots does not involve dislocation, which is supported by intense PL [15].

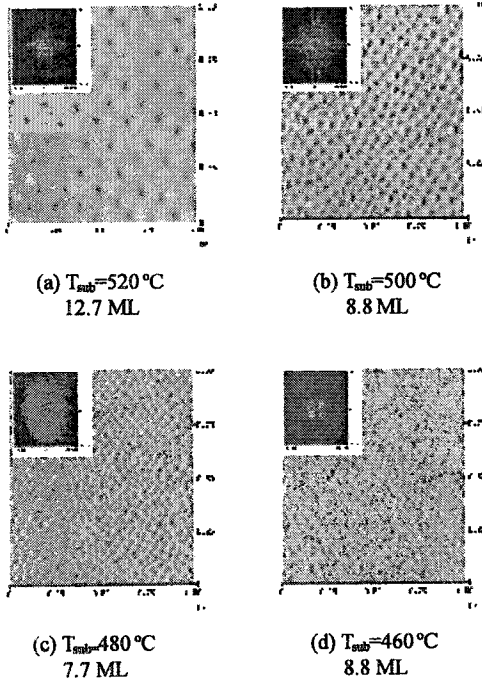


Figure 1. AFM images of $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$ grown on $\text{GaAs}(311)\text{B}$ at different temperatures.

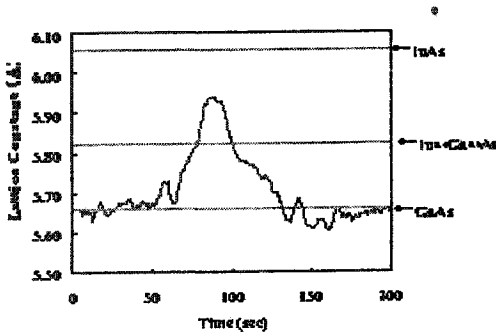


Figure 2. Changes in surface lattice constants during QD growth.

In order to understand the mechanism which prevents QDs from merging we investigated In distribution in $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$ QDs by the analysis of RHEED patterns [16]. Fig. 2 illustrates the change in the surface lattice constant during the growth of QDs. The growth rate and growth temperature were $0.1 \mu\text{m/h}$ and 500°C . The surface lattice constants for GaAs, InAs and $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$ which are indicated by arrows in the figure were obtained by measurement spacing between the diffraction patterns of thick films of GaAs, InAs and $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$. The lattice constant of the growing surface is shown on the left axis. During the RHEED measurement, the Ga shutter and the As shutter were opened, while the In shutter was opened at $t = 0$ and closed at $t = 80$ s. When the In shutter was opened the surface lattice constant increased with a delay and greatly exceeded the nominal value for $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$. When the In shutter was closed the RHEED separation returned to the value of GaAs.

If the dot surface consists of exactly $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$, the lattice constant should be less than the value of $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$ because the QDs are

constrained laterally. This result indicates that In distribution in QDs is not homogeneous and the dot surface is In rich. Auger analysis also shows the inhomogeneous distribution of In [16]. There may be two mechanisms which

explain this phenomenon. One is In segregation and the other is spinodal phase separation.

In ternary or quaternary compounds there is an energetically unstable region (miscibility gap) where it is difficult to obtain uniform composition. The calculation of miscibility gaps for InGaAs ternary alloy have been performed by Stringfellow [17] and Onabe [18], and it has been shown that InGaAs is energetically unstable around In-composition of 0.4. The RHEED result that the surface lattice constant grown at 540 °C is less than that of bulk $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$ suggests that at this temperature, miscibility gap disappears and uniform ternary compounds were obtained. Thus, the phase separation arising from miscibility gap is a possible mechanism for prevention against coalescence of InGaAs QDs. The result that InAs QDs grown on GaAs(311)B form large islands with increasing the deposition thickness to 3.9 ML [16] supports this consideration.

Changing substrate temperature is one simple method to control QD size and density. Another method is to put a spacer layer in between substrate and dot layer. For device application we need to grow QDs on AlGaAs substrate which has larger band discontinuity than GaAs. It is difficult to get ordered QDs on AlGaAs with large Al composition. However, we can get well-ordered QDs with a spacer layer on AlGaAs. The dot size and density are changed by the spacer layer thickness.

3 Electronic state in high density quantum dots

We can expect strong lateral coupling between QDs shown in Fig. 1(d). The quantum dot wavefunctions can be well delocalized as the surrounding barrier becomes thin and low, which results in the formation of extended miniband in the QDs system [19]. The extreme of the QDs ensemble is two dimensional quantum dot superlattice. However, we cannot avoid formation of some large islands which have lower energy levels than the extended state. Therefore, we need to treat the QD ensemble as a disordered system containing extended states and localized states.

The extended states originate from the strong coupling of uniform QDs. The localized states come from large islands that are excluded from the coupling due to much different size and energy. If this model is appropriate, we can expect a sharp decrease of the PL decay time at the bottom of the miniband (mobility edge) which separates the extended states from the localized states, as generally observed in conventional disordered system [20].

Fig. 3(a) shows the dominant PL decay time as a function of photon energy obtained at 1 W/cm^2 excitation. The excitation-dependent cw PL spectra are also shown for reference. A clear blue shift of the peak energy as well as a significant broadening of the line width is observed above the critical value between 0.12 and 0.52 W/cm^2 . Above this value the emission from the miniband begins to appear. Remarkably, a sharp decrease of the decay time from 2.5 ns to 25 ps is found at 1.290 eV. This energy position is attributed to the mobility edge. Fig. 3(b) and 3(c)

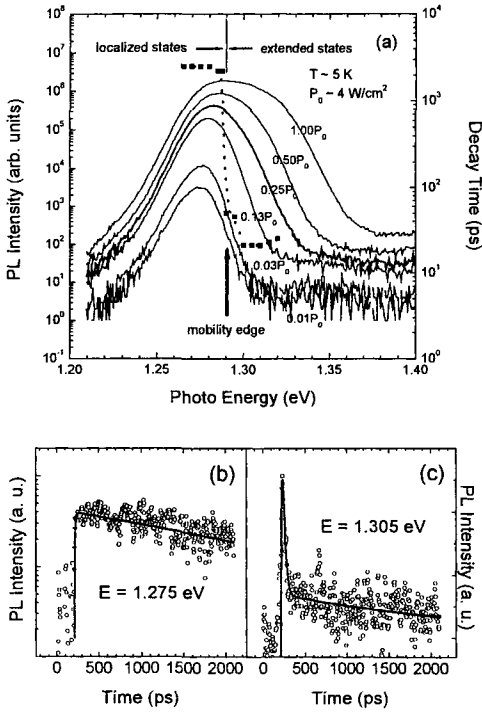


Figure 3. (a) PL decay time vs photon energy measured at 1 W/cm^2 (square dots). PL spectra (cw) at different excitation are also shown. (b) and (c) are typical PL transients for the localized and extended states.

were confirmed from a different point of view. The in-plane transport changes from hopping to resonant tunneling as the interdot distance is reduced [22]. The representative photocurrent-voltage curves for different samples measured at 4.5 K with irradiation intensity of 145 mW/cm^2 are shown in Fig. 4. A low pass filter with the cutoff at 850 nm was used to populate the QD layer and to suppress the excitation in GaAs matrix. Firstly, the photocurrent of the control sample (No. 4) which has no QD layer is much weaker than the other three samples with QDs. A $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}$ QD ensemble with quite inhomogeneous dot size shows hopping transport between the localized QD-state, which corresponds to No. 2 and No. 3. In the high-density ordered QDs array (No. 1), negative differential resistance (NDR) was observed. More important point is that the temperature dependence of photocurrents is opposite in the voltage ranges less than and more than the onset of NDR. At the voltage less than the onset voltage of NDR, the photocurrent decreases with temperature, while at the voltages higher than the onset the photocurrent increases with temperature. So, the conduction in the low voltage range is ascribed

show examples of the slow PL transient and the fast transient, which are typical for localized states and extended states, respectively.

These experimental observations justify the fact that the PL below the critical excitation intensity is dominated by isolated large islands and the excitons begin to populate the miniband with increasing excitation density. The PLE signal (not shown) of the strongly coupled QDs shows absorption edge which does not change with a change in the detection energy. The energy of the absorption edge corresponds to the energy of the mobility edge. On the other hand, the PLE signal of the low-density weakly coupled QDs shows a shift of absorption edge when the detection energy is changed, which is generally observed in isolated QDs [21].

These electronic structures

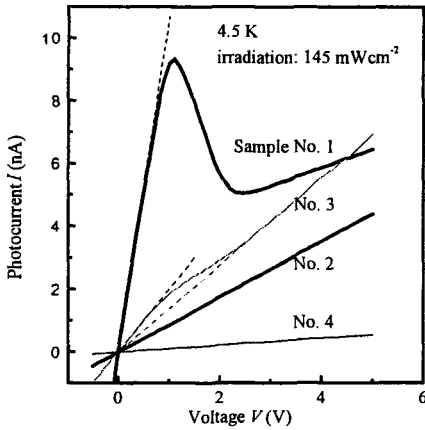


Figure 4. The in-plane photocurrent vs applied voltage for different samples.

temperatures. These QD arrays do not merge due to inhomogeneous distribution of In in the QDs. Lateral coupling between QDs which resulted in formation of miniband is confirmed in high-density closely packed QD arrays by distinct PL transient, PLE and photoconductivity. The formation of miniband is the first step for realization of 2-D or 3-D QD superlattices. However, more ordered QD arrays are needed to realize quantum dot superlattices where we can observe the effects of the periodic structures.

4 Acknowledgements

Many thanks go to Mr. Akhane H., Dr. Lan S. and Dr. Song H who performed experimental part of this work.

This work was supported in part by a Grant-in-Aid for the Scientific Research Project on the Priority Area of "Single Electron Devices and Their High Density Integration" from the Ministry of Education, Science, Sports and Culture and by the Project of "Analysis and Control of Self-Organization Mechanism of Substance and Materials" from the Science and Technology Agency. And also it is partly supported by the "Research for the Future" Program from JSPS (RFTF97P00106).

References

1. Solomon G. S., Trezza J. A., Marshall A. F., Harris J. S., *Phys. Rev. Lett.* **76** (1996) 952.
2. Sugiyama Y., Nakata Y., Futatsugi T., Sugawara M., Awano Y., Yokoyama N., *Jpn. J. Appl. Phys.* **36** (1997) L158.

to miniband transport. Over the onset of NDR a similar hopping conduction as that of isolated QDs was observed suggesting that the extended miniband is destroyed by an electric field as low as 10 Vcm^{-1} . This result suggests an electric field induced metal-insulator transition.

In summary, InGaAs QD arrays are fabricated on GaAs(311)B substrates by H-MBE. By changing the growth temperature from 540°C to 460°C , the dot density is changed from 10^9 cm^{-2} to 10^{11} cm^{-2} accompanied by a change in dot size from 120 nm to 30 nm . In particular, high-density closely packed QDs have been achieved at low growth

3. Nozel R., Temmyo J., Tamamura T., *Nature* **369** (1997) 131.
4. Murray C. B., Kagan C. R., Bawendi M. G., *Science* **270** (1995) 1335.
5. Springhiz G., Holy V., Pinczolis M., Bauer G., *Science* **282** (1998) 743.
6. Venezuela P., Tersoff J., Floro J. A., Chason E., Follstaedt D. M., Feng Liu Lagally M. G., *Nature* **397** (1999) 678.
7. Takeuchi A., Nakata Y., Muto S., Sugiyama Y., Inata T., Yokoyama N., *Jpn. J. Appl. Phys.* **34**(1995) L405.
8. Takeuchi A., Nakata Y., Muto S., Sugiyama Y., Usuki T., Nishikawa Y., Yokoyama N., Wada O., *Jpn. J. Appl. Phys.*, **34** (1995) L1439.
9. Kawabe M., Chun Y. J., Nakajima S., Akahane K., *Jpn. J. Appl. Phys.* **36** (1997) 4078.
10. Sugaya T., Kawabe M., *Jpn. J. Appl. Phys.* **30** (1991) L402.
11. Chun Y. J., Okada Y., Kawabe M., *Jpn. J. Appl. Phys.* **35** (1996) L1689.
12. Androussi Y., Lefebvre A., Courboulos B., Grandjean N., Massies J., Bouhacina T., Aime J. P., *Appl. Phys. Lett.* **65** (1994) 1162.
13. Shchunkin V. A., Lendentsov N. N., Kop'ev P. S. Bimberg D., *Phys. Rev. Lett.* **75** (1995) 2968.
14. Guha S., Maduhukar A. Rajkumar K. C., *Appl. Phys. Lett.* **57** (1990) 2110.
15. Kawabe M., Akahane K., Lan S., Ogino K., Okada Y. Koyama H., *Jpn. J. Appl. Phys.* **38** (1999) 491.
16. Akahane K., Kawamura T., Okino K., Koyama H., Lan S., Okada Y., Kawabe M., *Appl. Phys. Lett.* **73** (1998) 3411.
17. Stringfellow G. B., *J. App. Phys.* **54** (1983) 404.
18. Onabe K., *Jpn. J. Appl. Phys.* **21** (1982) L323.
19. Lan S., Akaahane K., Song H. Z., Okada Y., Kawabe M., Nishimura T. Wada O., *Phys. Rev. B* **61** (2000) 16847.
20. Permogorov S., Rezmitsky R., *J. Lumin.* **52** (1992) 201 and references therein.
21. Nishikawa S., Lan S., Wada O., Nishimura T., Akahane K. Kawabe M. In *The 7th Intern. Workshop on Femtosecond Technology* (Tsukuba, Japan, 2000) 195.
22. Markovich G., Collier C. P., Heath J. R., *Phys. Rev. Lett.* **80** (1998) 3807.

MULTIEXCITON DYNAMICS OF GaAs SINGLE QUANTUM DOTS

K. EDAMATSU, C. WATATANI, T. ITOH, S. SHIMOMURA, S. HIYAMIZU

*Graduate School of Engineering Science, Osaka University
Toyonaka 560-8531, Japan*

E-mail: eda@mp.es.osaka-u.ac.jp

We have investigated the multiexciton states confined in a single GaAs/AlGaAs quantum dot (QD) grown on a GaAs (411)A surface by means of micro-photoluminescence and excitation spectra. We observed three types of photoluminescence lines, originating from one exciton, biexciton, and multiple exciton states confined in the QD. We also observed sharp resonances in the excitation spectra, not only in Stokes side but also in anti-Stokes side. The unusual anti-Stokes resonance indicates the efficient energy transfer process probably driven by Auger excitation.

1 Introduction

Recent development of single quantum dot (QD) spectroscopy has revealed many interesting and important properties of semiconductor quantum dots such as sharp homogeneous linewidth [1], very long coherence time [2], luminescence intermittency [3], anti-bunched photon emission [4]. Because of the three-dimensional quantum confinement, the interaction between electrons, holes, and excitons confined in a QD is considerably enhanced, and thus strong optical nonlinearity is expected [5]. Recently, excitation-intensity-dependent luminescence lines that are the direct indication of the discrete multiple exciton states have been reported [6]. In this paper, we report the micro-photoluminescence (micro-PL) spectra from a GaAs/AlGaAs quantum dot grown on the (411)A surface of a GaAs substrate, and discuss the relation between the observed PL lines and the confined multiexciton states in the QD [7]. Also we report on anomalous anti-Stokes luminescence that is probably caused by efficient Auger excitation process.

2 Experimental procedure

The sample of GaAs quantum dots is based on a GaAs/Al_{0.3}Ga_{0.7}As quantum well (QW) made by a molecular beam epitaxy method [8]. Under an appropriate growth condition with relatively small As flux, triangular pyramidal-shaped structure is grown on a GaAs (411)A surface. Fig. 1(a) shows the atomic force microscope (AFM) image of the sample surface. By growing a quantum well over the pyramid, the thicker area of the well is formed on a slope of the pyramid, as shown in

Fig. 1(b). This area contains a number of QD structures in which the excitons are confined, as described later. It is plausible that these QDs originate from a certain fluctuation of the well thickness in the pyramidal structure, just like as QDs fabricated by growth-interruption techniques [1].

From the cross-sectional scanning electron microscope image, the lateral size of the thicker area is estimated to be ≈ 500 nm, and it is almost independent of the thickness of the GaAs layer. The density of the pyramid is as low as 10^7 cm $^{-2}$, so that we can resolve the luminescence from a single pyramidal structure using a conventional microscope objective lens. We used two excitation light sources depending on the measurements. For the band-to-band excitation of the barrier and well layers, we used the second harmonic light of a picosecond Ti:Sapphire laser (wavelength = 395 nm, repetition rate 82 MHz, pulse width 10 ps) as the excitation source. By use of the pulsed excitation, multiple excitons can be created in a QD under relatively small mean power. For the resonant excitation of the QD, we used a continuous wave Ti:Sapphire laser.

For the micro-PL measurement, the excitation beam was focused and the photoluminescence was collected by an objective lens (x50, N.A.=0.42). The sample was mounted on the cold-finger of a cryostat and cooled down to 3.3 K. For the band-to-band excitation, the collected light was dispersed by a single monochromator (focal length = 50 cm), and detected by a LN-cooled CCD camera. In the case of the resonant excitation close to the detection wavelength, a triple monochromator (focal length = 64 cm) was used to eliminate the intense scattering of the excitation light.

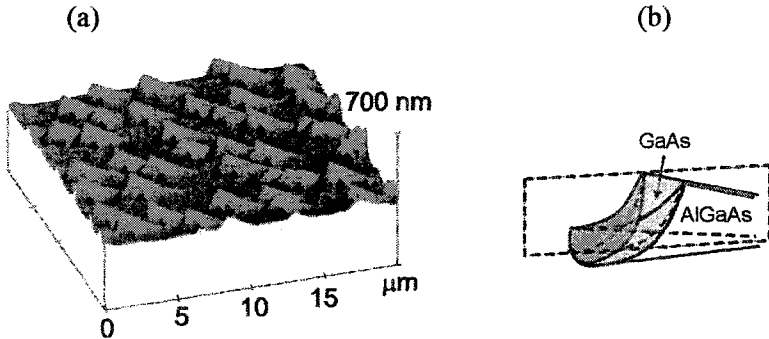


Figure 1. (a) AFM image of the GaAs (411)A surface used as a substrate of the sample. (b) Schematic drawing of the GaAs/AlGaAs quantum well structure overcoated on the pyramidal structure.

3 Results and discussion

3.1 Micro-PL spectra and multiexciton states in the QD

Fig. 2 shows the micro-PL spectra from a single pyramidal structure for various excitation power. At low excitation power, we observed a bunch of sharp luminescence lines, indicated by (a) in Fig. 2, around 1.588 eV. The spectral widths of these lines are estimated to be $\approx 150 \mu\text{eV}$ after the correction of the experimental spectral resolution. We observed at least two luminescence lines from a single pyramidal structure at very low excitation power. This indicates that a number of QDs are formed in a single pyramid, as described above.

At higher excitation power, additional bunches of luminescence lines, indicated by (b) and (c), appear in lower (1.585 eV) and higher (1.603 eV) energy side of the lines (a), respectively. Fig. 3 shows the excitation power dependences of the luminescence intensities (a), (b), and (c) in Fig. 2. The intensities of lines (a) linearly increase at low excitation power and tend to saturate at higher excitation. On the other hand, lines (b) and (c) increase superlinearly with the increase of excitation power. At the lowest excitation power (56 mW/cm^2) we have measured,

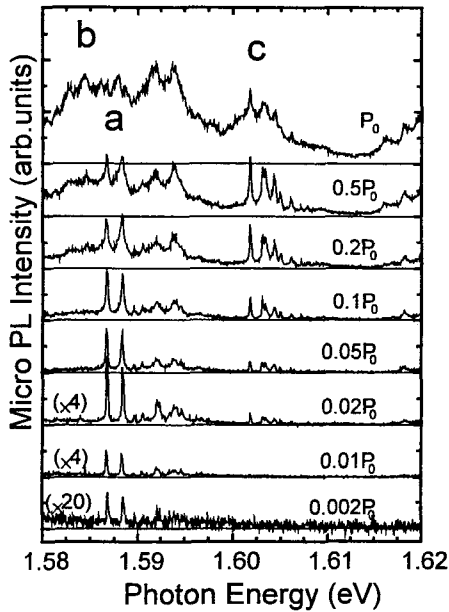


Figure 2. Micro-PL spectra of the GaAs quantum dot contained in a single pyramidal structure under various excitation power at 3.3 K. $P_0=28 \text{ W/cm}^2$.

the average number of excitons created in a QD is estimated about 0.01. In this region of excitation power, the luminescence only from the lowest state of the confined exciton is expected to be observed.

For the higher excitation density, multiple excitons are simultaneously created in a QD, and thus luminescence originating from not only the lowest but also from the higher excited states of the confined exciton could be observed. Solid curves in Fig. 3 represent the stochastically calculated number of the QDs that contributes to the luminescence (a), (b) and (c). Here, we assume that the initial distribution of the number of excitons n created by an excitation pulse in a QD follows the Poisson distribution P_n . Taking into account the cascade annihilation of the excitons, the number of QDs that emit the luminescence via the de-excitation from N to $N-1$ exciton states is expected by

$$I_N \propto \sum_{n=N}^{\infty} P_n. \quad (1)$$

The calculated intensities are shown by solid curves indicated by I_N ($N=1, 2, 3$) in Fig. 3. The luminescence intensity (a) is well reproduced by I_1 ,

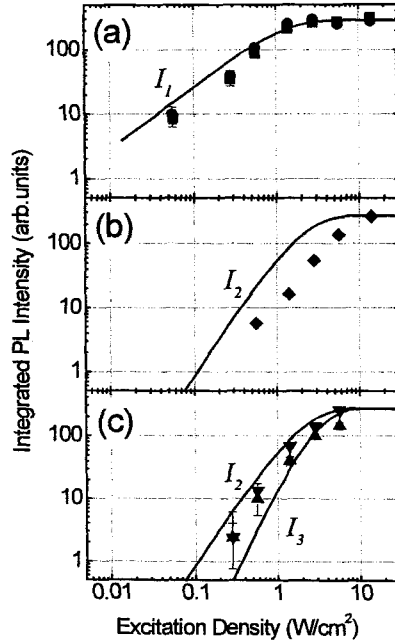


Figure 3. Excitation power dependences of the luminescence intensities. Solid curves are the calculated values from Eq. (2) in the text. Curves I_1 , I_2 and I_3 indicate the calculated intensities in the cases of one, two and three excitons are initially created in a QD, respectively.

whereas (b) is reproduced by I_2 and (c) follows I_2 or I_3 . These results suggest that the lines (a), (b) and (c) originate from the lowest state of one exciton, biexcitonic state (two excitons) and multiple excitons state in a QD, respectively. According to the Pauli principle, the lowest excitonic state in a QD can be occupied by up to two excitons. Therefore, the luminescence from the higher excited state appears when multiple excitons are simultaneously created in a QD. This behavior is qualitatively explained by the recent theoretical calculation [9].

With raising temperature, the PL lines in Fig. 2 exhibit considerable broadening and a slight red shift. The spectral linewidths (FWHM) of the PL lines (a) in Fig. 2 at relatively low excitation density (0.28 W/cm^2) are plotted in Fig. 4 as a function of temperature. We expect the thermal broadening is caused by the transition from the lowest to a certain higher excited state via one-phonon absorption [1]. In this model, the luminescence linewidth from the lowest excited state Γ is written as

$$\Gamma(T) = \Gamma_0 + \gamma \left[\exp\left(\frac{\Delta E}{k_B T}\right) - 1 \right]^{-1}, \quad (2)$$

where Γ_0 is the radiative linewidth of the lowest excited state, γ and ΔE are the transition probability and energy separation between the lowest and higher excited states, respectively.

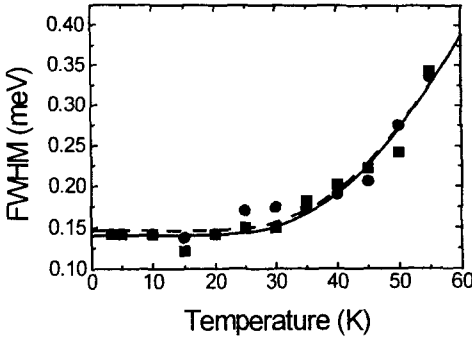


Figure 4. Temperature dependence of the luminescence linewidth. Solid and broken curves are calculated values assuming Eq. (2) in the text.

By fitting this equation to the experimental result, we obtained the value of $\Delta E \approx 15 \text{ meV}$. This value is almost consistent with the energy difference between lines (a) and (c) in Fig. 2. Thus, the temperature dependence of the spectral linewidth also supports our assignment that lines (a) and (c) originate from the lowest and higher excited states of the QD, respectively.

3.2 Excitation Spectra and Energy Transfer Process

The micro-PL spectrum observed from a single pyramidal structure, which is different from that measured for Fig. 2, is shown in Fig. 5(c). Unlike the dot used for the measurement of Fig. 2, this dot did not exhibit any additional luminescence lines that correspond to the lines (c) in Fig. 2, even if we excite the dot under the same condition as in Fig. 2.

The difference in the optical properties is probably attributed to the difference in physical size and shape of the two dots. Also note that the excitation in Fig. 5 was

made with a continuous wave laser, while the excitation in Fig. 2 was performed with a picosecond pulsed laser. The excitation (micro-PLE) spectra detected at four luminescence lines (#1 to #4 in Fig. 5(c)) are shown in Fig. 5(a, b). The PLE spectra have several sharp peaks reflecting the discrete energy levels of the QD. Close similarity between the PLE spectra for #1 and #4, and for #2 and #3, suggests that the luminescence #1 and #4 originates from an identical dot, and #2 and #3 from another dot in a pyramid. In addition, for both cases, quasi-continuous excitation band appear above 1.594 eV. This continuum suggests that the dots are surrounded by the two-dimensional states of the GaAs layer. Furthermore, it is noteworthy that the lines #3 and #4 have the sharp anti-Stokes resonance at the energy position of the luminescence lines #2 and #1, respectively, as indicated by the open triangles. To our knowledge, this is the first observation of such distinct anti-Stokes resonance in the luminescence excitation spectra of any quantum dots.

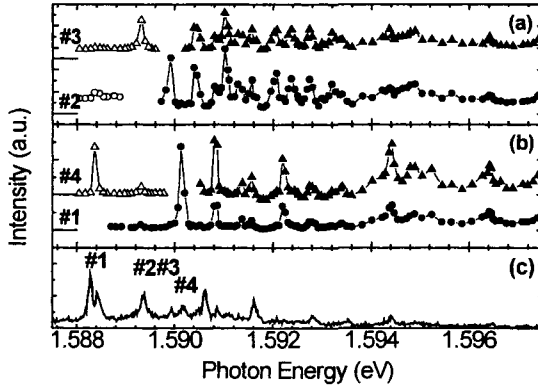


Figure 5. Micro-PLE (a, b) and micro-PL (c) spectra of the GaAs QDs at 3.8 K. The micro-PL spectrum was taken under excitation at 1.687 eV, 5.5 W/cm². The micro-PLE spectra were detected at the four sharp lines (#1–#4) indicated in the micro-PL spectrum.

Fig. 6 shows the micro-PL spectra for various excitation power under resonant excitation at the energy position indicated by the downward arrow, which corresponds to the PL line #4 in Fig. 5(c). One can see that several PL lines appear on both the Stokes and anti-Stokes sides. The energy separation of the anti-Stokes PL ranges over more than 6 meV. Because the spectra were taken at low temperature (3.8 K), the anti-Stokes PL cannot originate from thermal excitation. From the analysis of the excitation power dependence of the luminescence intensity, we found that the anti-Stokes PL line indicated by the filled circle in Fig. 6 arises when at least two excitons are created in the QD. Thus, we suppose that the anti-Stokes PL line is caused by Auger excitation of the dots, which often results in the luminescence intermittency and photo-darkening effects [3]. On the other hand,

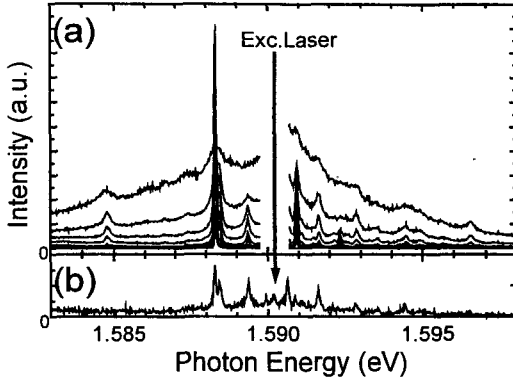


Figure 6. (a) Micro-PL spectra under the resonant excitation at 1.5902 eV (indicated by the downward arrow). The excitation power (P_{exc}) varied from 11 to 5500 W/cm² from the lower to upper curves. (b) micro-PL spectrum under excitation at 1.687 eV, and $P_{\text{exc}} = 5.5$ W/cm².

since the Stokes PL line (square in Fig. 6) appears when one exciton is created in the QD, it is attributed to the recombination of the lowest excitonic state of the QD that is initially excited to the higher state. Furthermore, the PL line (triangle in Fig. 6) that appears under the high excitation density arises when two excitons are created in the QD. Thus, this line is attributed to the emission from the biexciton in the QD. The binding energy of the biexciton is 3.4 meV, which is comparable to the previously reported value (~ 4 meV) for GaAs QDs [10]. The coexistence of the Auger excitation and the biexciton luminescence in a QD is an interesting and important problem to discuss in further investigations.

4 Conclusion

We have investigated the micro-PL and micro-PLE spectra of the GaAs/AlGaAs quantum dots included in a pyramidal structure formed on a GaAs (411)A surface. We observed a number of luminescence lines originating from an exciton, biexciton, and multiple exciton states confined in the single quantum dot, depending on the excitation power. The micro-PLE spectra showed sharp resonant lines both in Stokes and anti-Stokes sides. The anti-Stokes lines are probably attributed to efficient Auger excitation process in the dot.

5 Acknowledgements

This work was supported by Grant-in-Aid for COE Research (10CE2004) and Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References

1. Gammon D., Snow E. S., Shanabrook B. V., Katzer D. S., Park D., *Science* **273** (1996) 87.
2. Bonadeo N. H., Erland J., Gammon D., Park D., Katzer D. S., Steel D. G., *Science* **282** (1998) 1473.
3. Nirmal M., Dabbousi B. O., Bawendi M. G., Macklin J. J., Trautman J. K., Harris T. D., Brus L. E., *Nature* **383** (1996) 802; Efros Al. L., Rosen M., *Phys. Rev. Lett.* **78** (1997) 1110.
4. Michler P., Imamoğlu A., Mason M. D., Carson P. J., Strouse G. F., Buratto S. K., *Nature* **406** (2000) 968.
5. Schmitt-Rink S., Miller D. A. B., Chemla D. S., *Phys. Rev. B* **35** (1987) 8113; Hanamura E., *Phys. Rev. B* **37** (1988) 1273; Banyai L., Hu Y. Z., Lindberg M., Koch S. W., *Phys. Rev. B* **38** (1988) 8142; Hu Y. Z., Lindberg M., Koch S. W., *Phys. Rev. B* **42** (1990) 1713.
6. Bayer M., Stern O., Hawrylak P., Faraed S., Forchel A., *Nature* **405** (2000) 923.
7. Watatani C., Edamatsu K., Itoh K., Hayashi H., Shimomura S., Hiyamizu S., *Phys. Stat. Sol. (b)*, in press.
8. Hayashi H., Shimomura S., Hiyamizu S., unpublished.
9. Nair S. V., Masumoto Y., *J. Lumin.* **87-89** (2000) 437.
10. Brunner K., Abstreiter G., Bohm G., Tränkle G., Weimann G., *Phys. Rev. Lett.* **73** (1994) 1138.

INVITED

PHOTOREFLECTANCE INVESTIGATIONS OF LOW DIMENSIONAL SEMICONDUCTOR STRUCTURES

J. MISIEWICZ, G. SĘK

*Institute of Physics, Wrocław University of Technology
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

M. BAYER, A. FORCHEL

*Institute of Physics, University of Würzburg
Am Hubland, D-97074 Würzburg, Germany*

E-mail: jmis@if.pwr.wroc.pl

Photoreflectance spectroscopy on several low-dimensional structures has been presented. The optical transitions have been investigated in coupled $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum wells, double $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum wells and vertically coupled $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ double quantum dots as a function of the thickness and separating barrier layer. Transition and splitting energies versus barrier thickness have been obtained and compared with the results of the envelope function calculations.

1 Introduction

Modulation spectroscopy is the branch of optical spectroscopy that deals with the measurements and interpretation of changes in optical spectra of a sample which are caused by modifying in some way the measurement conditions. Photoreflectance (PR) is a contactless electromodulation technique where the modulation is caused by the photogenerated changes of the internal (built-in) electric fields. Modulation of the electric field is caused by photo-excited electron-hole pairs created by the pump source (usually laser) which is chopped with a given frequency. The perturbation, due to the changes of the electric field, causes modulation of the complex dielectric function, which can be directly related to the changes of the optical response, i.e. reflectivity. In PR, the normalised changes of the reflectivity coefficient are measured.

Since PR was first applied to multiple quantum well structures and heterojunctions in 1985 [1], it has become important in accumulation of band structure parameters of low-dimensional structures like single quantum wells (SQW), multiple quantum wells (MQW), superlattices (SL), heterojunctions (HJ), quantum wires (QWR) and quantum dots (QD) [2-11].

In the case of bound states like those in quantum wells or excitons, the modulating electric field does not accelerate charge carriers in the field direction

and the modulation is described on the base of quantum confined Stark effect in contrast to the bulk case modulation which is described by Franz-Keldysh effect.

2 Experimental details

A schematic diagram of the photorefectance apparatus is shown in Fig. 1. The

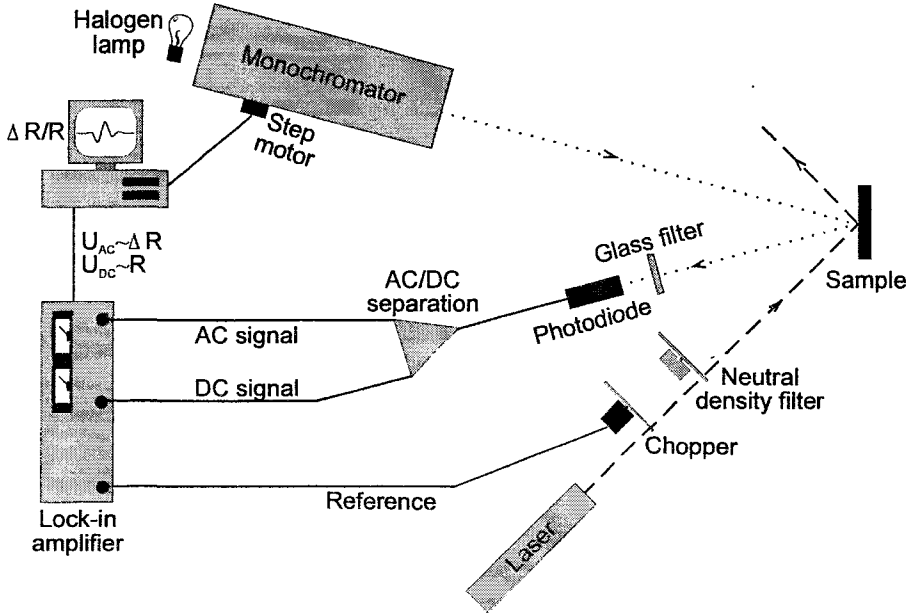


Figure 1. Schematic diagram of the apparatus for photorefectance measurements.

probe light is a monochromatic beam obtained from a lamp dispersed through a monochromator. The reflected probe beam is detected by a photomultiplier or a suitable photodiode. Modulation of the electric field in the sample is caused by the pump source (usually laser) which illuminates the same spot of the sample and is chopped at a certain frequency f_m . The light striking the detector contains two signals: a DC or average value $I_0 R$ (where I_0 is the intensity of the light impinging on the sample and R is the energetic reflectivity coefficient) and a modulated AC value $I_0 \Delta R$ varying with the frequency f_m (where ΔR is the change in reflectivity caused by a pump beam). Since it is the quantity $\Delta R/R$ that is interest, the common factor I_0 is eliminated. The signal is recorded by a personal computer using lock-in technique.

The samples investigated in this work were grown by MBE on semi-insulating (001) GaAs substrates. $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum well samples consisted of three or four 7.5 nm thick $\text{In}_{0.045}\text{Ga}_{0.955}\text{As}$ wells separated by 1, 3, 5 or 9 ML of GaAs.

$\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ double quantum wells are separated by 0, 1, 3 or 5 ML of AlAs barriers, and cladded between two 150 nm thick $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ and $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ layers. The double quantum dot structures consisted of two layers of self-assembled $\text{In}_{0.6}\text{Ga}_{0.4}\text{As}$ quantum dots separated by 3, 5 or 10 nm of GaAs.

3 Results and discussion

3.1 Coupled $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum wells

A photoreflectance spectrum for the case of four coupled quantum wells structure is shown in Fig. 2 [12]. We use the standard notation where H(L)mn denotes a transition from the m-th conduction subband to n-th valence subband of heavy (H) or light (L) hole character. For heavy holes, in addition to the parity allowed transitions with $m = n$ also some nominally forbidden transitions are observed. The H13 transition can be made allowed by band mixing [13-14] or by the finite barrier height, which induces different vanishing rates for electron and hole envelope functions into the wider-gap material, so that the resulting envelope function overlap integral is not zero [15]. The observation of parity forbidden transitions such as H12 or H21 can be explained as an effect of the valence band mixing [13-14], or due to random alloy fluctuations or the surface electric field, which destroys the symmetry of the system [16,17].

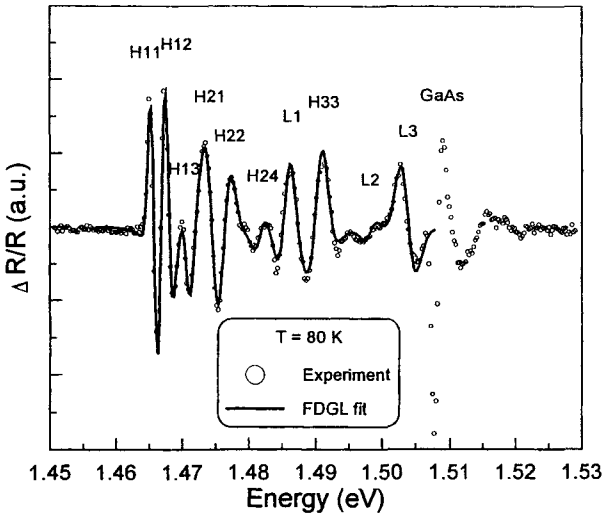


Figure 2. Photoreflectance spectrum of four coupled $\text{In}_{0.045}\text{Ga}_{0.955}\text{As}/\text{GaAs}$ quantum wells separated by 5ML of GaAs. Arrows indicate the experimental transition energies obtained from the least-square fit according to the first derivative of the Gaussian line shape.

The light hole transitions need to be discussed in more details. The axial component of strain present in $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers splits the valence band degeneracy and the light hole band edge moves to lower energies than the valence band edge in GaAs layers. Due to this effect, the $\text{In}_x\text{Ga}_{1-x}\text{As}$ material acts as a potential barrier for light holes. Therefore we interpret the transitions labelled LH1, LH2 and LH3 as involving the three lowest electron subbands in $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers and the single light hole subband in GaAs layers.

The observation of forbidden transitions H12 and H21 allowed obtaining the energy of the splitting between two lowest heavy hole and electron subbands, which value is related to the strength of the coupling between the wells. The values of the splitting energies have been obtained for samples with three and four quantum wells with barrier thickness changing from 1 to 9 ML. The splitting energy as a function of the barrier thickness is shown in Fig. 3. The energies from PR spectra have been compared with the results of envelope function calculations, in which full three- and four-well geometry have been modelled.

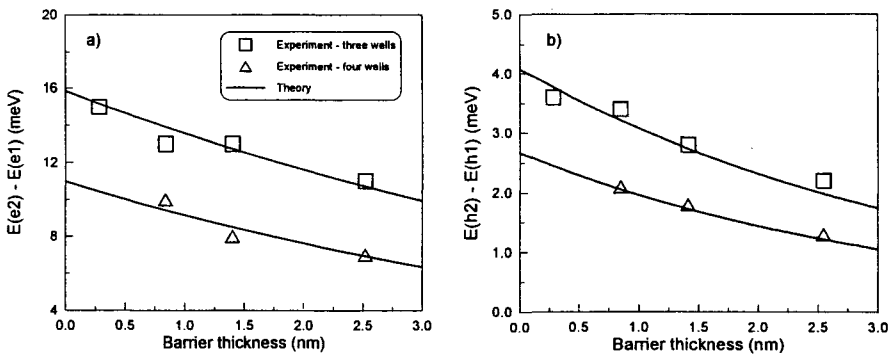


Figure 3. Splitting energy between two lowest a) electron and b) heavy hole levels for structures with three and four coupled quantum wells versus GaAs barrier thickness.

3.2 Coupled $\text{Al}_x\text{Ga}_{1-x}\text{As}$ /GaAs double quantum wells

Fig. 4 shows room temperature PR spectrum for $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}/\text{GaAs}$ DQW structure with 1 ML thick AlAs barrier [18]. The spectrum consists of two groups of PR resonances. The first one starting above the energy of GaAs-related feature is connected with transitions between the confined states in the DQW. The second one is related to transitions between confined states and resonant states in the quasi continuum region above the band edge of the $\text{Al}_{0.35}\text{Ga}_{0.7}\text{As}$ barrier.

The experimental energies of confined transitions were obtained from the least-square fitting procedure according for the first derivative of Gaussian line shape, the most appropriate profile of the PR signal in the case of transitions involving confined states at room temperature [2,3,5]. The transitions are labelled according to the notation used in Section 3.1, where H and L mean the transition for heavy and

light holes, respectively. The indexes s and a mean the transition between symmetric and antisymmetric states, respectively. The energies of the observed transitions were compared with the results of theoretical considerations for four samples with barrier thickness 1, 3 and 5 ML and for the sample without a barrier imitating the case of infinitely thin barrier.

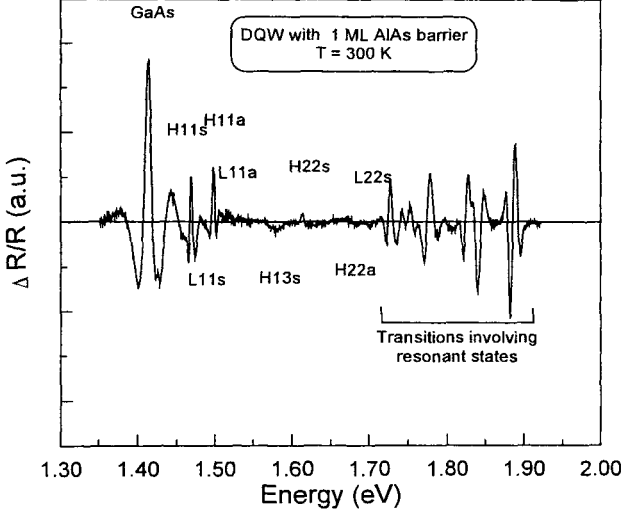


Figure 4. Room temperature PR spectrum of $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}/\text{GaAs}$ DQW structure with 1 ML AlAs barrier. Arrows indicate the energies of confined transitions [18].

We used effective mass approximation to calculate energy levels and envelope wave functions of the confined states in the investigated DQWs. In Fig. 5 the AlAs barrier width dependence of all observed confined transitions energies is shown. The solid lines are the theoretical curves and the circles are the experimental data. It can be clearly seen that with the increase of the AlAs barrier thickness coupling between the wells weakens and the splitting between the symmetric and antisymmetric transitions decreases. The transition energies tend toward the energies of the 7.5 nm well with infinitely thick barriers. It is also seen that the splitting energy between symmetric and antisymmetric transitions is smaller for heavy holes. This can be understood on the base of the following relation, which gives the splitting energy between the symmetric and antisymmetric single-particle states

$$\Delta_{a-s} = E_a - E_s = \frac{E}{\pi} \exp\left(-\sqrt{\frac{2mE}{\hbar^2}}L\right),$$

where E is the energy of electron or hole in the decoupled single quantum well, m is the electron/hole effective mass and L is the separating barrier width. We can see

that the splitting energy Δ_{a-s} is strongly dependent on the barrier width, the barrier height (via E) and the carrier mass. Hence, for different masses of holes the splitting has a different value.

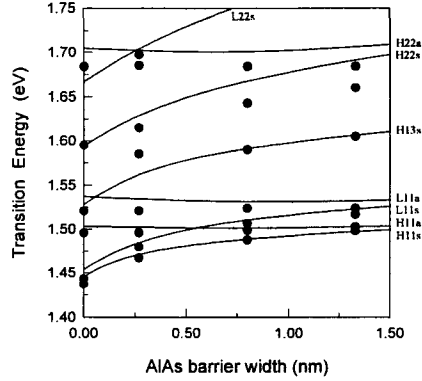


Figure 5. Dependence of the confined transition energies on the AlAs barrier thickness. Circles – experiment, solid lines – theory [18].

The experimental data agree quite well with the results of calculations. However, some discrepancies can be seen. The theory slightly overestimates the energies of transitions obtained from the experiment probably due to exciton binding energy, which was not included into the calculations.

The barrier thickness dependence of the splitting energy between the symmetric and antisymmetric transitions is shown in Fig. 6.

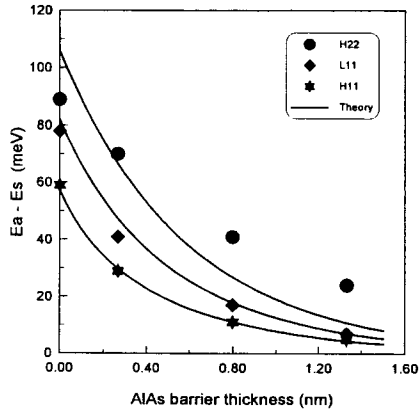


Figure 6. The difference energy between antisymmetric and symmetric transitions versus barrier thickness. Symbols – experiment, solid lines – theory.

For the lowest H11 and L11 transitions very good agreement has been obtained. The disagreement for H22 transitions can be caused by the difference in the exciton binding energy of s and a excitons, which have not been included.

The high-energy part of the spectrum in Fig. 4 looks like a superposition of many resonances. To resolve them and to analyse in details we performed the measurements in this region at 2 K. The comparison of low temperature PR and reflectivity spectra for sample with 1 ML AlAs barrier is presented in Fig. 7. Below

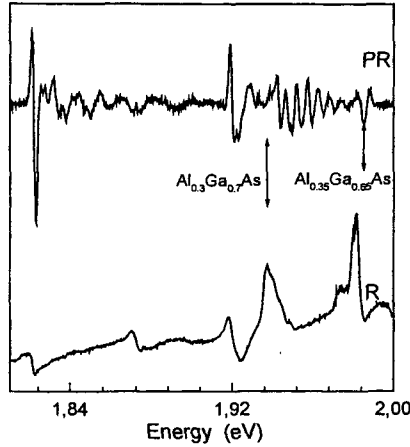


Figure 7. Comparison of low temperature R and PR spectra in the region of resonant state transitions recorded at 2 K for DQW with 1 ML AlAs barrier.

the band gap energy of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ barrier several transitions involving resonant states are seen. In the region between the energies of both barriers the transitions between the very dense ladder of levels in the broad step above the edge of the conduction and valence band of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ are observed in the PR spectrum as a quasi-oscillatory part. The comparison shows that the modulation spectrum gives much more information than standard reflectivity at the same measurement conditions.

3.3 Coupled $\text{In}_x\text{Ga}_{1-x}\text{As}$ /GaAs double quantum dots

In Fig. 8, we show the 10 K PR spectrum of double $\text{In}_{0.6}\text{Ga}_{0.4}\text{As}$ quantum dot structures for the case of 3 nm thick GaAs separating layer [19]. The PR spectrum can be divided into two parts. The strong feature at the 1.52 eV is related to the GaAs band gap transition. The low energy part exhibits several transitions related to the QDs and to the wetting layer (WL). To extract the transition energies in QDs and WL the spectra have been fitted using the first derivative Gaussian line shape (FDGL) describing inhomogeneously broadened PR features for confined transitions [2,3,5].

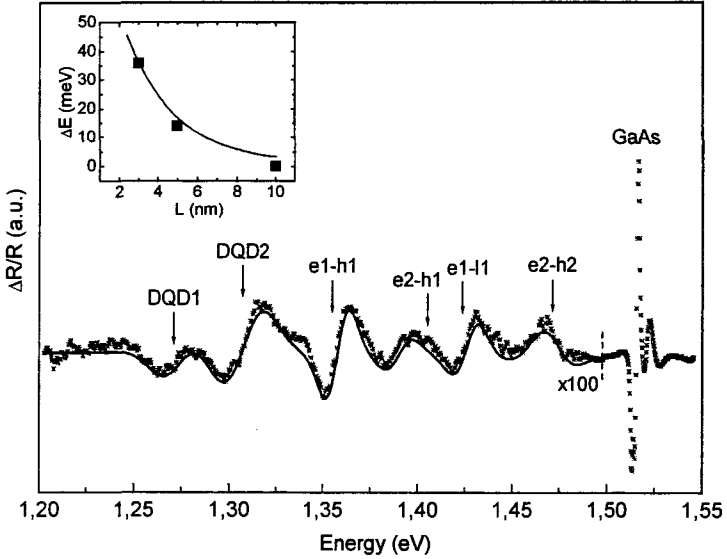


Figure 8. PR spectrum of double quantum dot structure with separating GaAs layer of 3nm: symbols – experiment at 10 K, solid line – first derivative Gaussian line shape fit. The inset shows the dependence of the energy difference between the two lowest heavy hole transitions versus the thickness L of the GaAs separating layer: squares – experiment, solid line – theory.

The states of DQD system are also split into two levels but in this case we can not call them symmetric and antisymmetric because the three dimensional wave functions are more complicated in the coupled lens-shaped dots. For DQD transitions two main effects are observed. First of all, the transition energy of the QD-related features decreases with decreasing the GaAs barrier. Secondly, the energy difference ΔE between the first two allowed transitions increases with the decrease of separating layer thickness. The dependence of ΔE on the thickness of GaAs layer separating two quantum dot sheets is presented in the inset of Fig. 8 for samples with 3, 5 and 10 nm of GaAs spacer. This demonstrates a strong dependence of the splitting on the barrier width. The value of ΔE is the sum of the electron and heavy hole splitting energies, but reflects mainly the former one due to the much larger heavy hole effective mass (much weaker heavy hole splitting). For the case of 10 nm thick separating layer no splitting has been observed. Therefore, in a first approximation the dot-dot interaction can be neglected and almost uncoupled case is achieved.

4 Conclusions

Photoreflectance spectra of coupled $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum well and $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ quantum dot structures have been measured and interpreted. We have obtained the energies of optical transitions between the split levels, due to the coupling, and compared them to the results of envelope function calculations in the effective mass approximation. We have investigated the influence of the coupling strength, in quantum wells of different material systems and in vertically coupled quantum dots, on the optical transitions including those between excited states up to the states above the band edge of the barrier. The dependences of the splitting energies on the thickness of the separating barrier for coupled wells and dots have been derived.

5 Acknowledgements

This work was supported in part by the Centre for Advanced Materials and Nanotechnology of Wrocław University of Technology and by the Polish Committee for Scientific Research, Grant No. 8 T11B 010 18.

References

1. Glembocki O. J., Shanabrook B. V., Bottka N., Beard W. T., Comas J., Photoreflectance characterisation of interband transitions in $\text{GaAs}/\text{AlGaAs}$ multiple quantum wells and modulation doped heterojunctions, *Appl. Phys. Lett.* **46** (1985) pp. 970-972.
2. Pollak F. H., Modulation spectroscopy of semiconductors and semiconductor microstructures. In *Handbook on semiconductors*, ed. by Moss T. S. (Elsevier Science, North Holland, Amsterdam, 1994) pp. 527-635.
3. Misiewicz J., Sitarek P., Sęk G., Introduction to the photoreflectance spectroscopy of semiconductor structures, (Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, 1999).
4. Misiewicz J., Sęk G., Sitarek P., Photoreflectance spectroscopy applied to semiconductors and semiconductor heterostructures, *Optica Applicata* **29** (1999) pp. 327-363.
5. Misiewicz J., Sitarek P., Sęk G., Photoreflectance spectroscopy of low-dimensional semiconductor structures, *Opto-electronics Rev.* **8** (2000) pp. 1-24.
6. Sęk G., Misiewicz J., Radziejewicz D., Tłaczała M., Panek M., Korbutowicz R., Study of the nature of light hole excitonic transitions in $\text{InGaAs}/\text{GaAs}$ quantum well, *Vacuum* **50** (1998) pp. 199-201.

7. Sęk G., Ciorga M., Misiewicz J., Radziejewicz D., Korbutowicz R., Panek M., Tłaczała M., Optical investigations of strained InGaAs quantum wells, *Adv. Mater. Opt. Electron.* **7** (1998) pp. 307-310.
8. Sitarek P., Sęk G., Misiewicz J., Cheng T. S., Investigations of AlGaAs/GaAs multiple quantum wells, *Vacuum* **50** (1998) pp. 203-205.
9. Sęk G., Misiewicz J., Ryczko K., Kubisa M., Heinrichsdorff F., Stier O., Bimberg D., Room temperature photoreflectance of MOCVD-grown InAs/GaAs quantum dots, *Solid State Commun.* **110** (1999) pp. 657-660.
10. Sęk G., Ryczko K., Misiewicz J., Fischer M., Reinhardt M., Forchel A., Photoreflectance spectroscopy of InGaAsN/GaAs quantum wells grown by MBE, *Thin Solid Films* **380** (2001) pp. 240-242.
11. Sęk G., Nowaczyk M., Bryja L., Ryczko K., Misiewicz J., Bayer M., Koeth J., Forchel A., Magneto-photoreflectance of the above barrier state transitions in GaAs/Al_{0.3}Ga_{0.7}As double quantum wells, in *Proc. of the International Conference on the Physics of Semiconductors, Osaka'2000*, (2000), in press.
12. Sęk G., Ryczko K., Misiewicz J., Bayer M., Wang T., Koeth J., Forchel A., Photoreflectance spectroscopy of coupled In_xGa_{1-x}As/GaAs quantum wells, *Thin Solid Films* **364** (2000) pp. 220-223.
13. Wang T., Bayer M., Forchel A., Effect of the hole subband mixing on the spin splitting of heavy-hole excitons in coupled In_{0.045}Ga_{0.955}As/GaAs double quantum wells, *Phys. Rev. B* **58** (1998) pp. R10183-R10186.
14. Miller R. C., Gossard A. C., Sanders G. D., Chang Y. C., Schulman J. N., New evidence of extensive valence-band mixing in GaAs quantum wells through excitation photoluminescence studies, *Phys. Rev. B* **32** (1985) pp. 8452-8454.
15. Fang Z. M., Persson A., Cohen R. M., Allowed 3h-1e transition in semiconductor quantum wells, *Phys. Rev. B* **37** (1988) pp. 4071-4075.
16. Devine R. L. S., Moore W. T., Photoluminescence of InGaAs/GaAs pseudomorphic single quantum wells: effect of excitation intensity, *Solid State Commun.* **65** (1988) pp. 177-179.
17. Moore K. J., Duggan G., Raukema A., Woodbridge K., Miniband dispersion in InGaAs-GaAs strained-layer superlattices, *Phys. Rev. B* **42** (1990) pp. 1326-1331.
18. Sęk G., Ryczko K., Ciorga M., Bryja L., Kubisa M., Misiewicz J., Bayer M., Koeth J., Forchel A., Optical investigation of coupled GaAs/Al_{0.3}Ga_{0.7}As double quantum wells separated by AlAs barrier. In *Proc. of the NATO Advanced Research Workshop on Optical Properties of Semiconductor Nanostructures, Jaszwieć'1999*, ed. by Sadowski M. L. et al. (Kluwer Academic Publishers, The Netherlands, 2000) pp. 91-95.
19. Sęk G., Ryczko K., Misiewicz J., Bayer M., Klopff F., Reithmaier J. P., Forchel A., Photoreflectance spectroscopy of vertically coupled InGaAs/GaAs double quantum dots, *Solid State Commun.* **117** (2001) pp. 401-406.

THERMOELECTRIC PROPERTIES OF CHAOTIC QUANTUM DOTS

H. BUHMANN, S. MAKSIMOV, L. W. MOLENKAMP

*Physikalisches Institut, Universität Würzburg
Am Hubland 97074 Würzburg, Germany*

E-mail: hartmut.buhmann@physik.uni-wuerzburg.de

Thermopower measurements can often provide the transport physicist with information that is complementary to results obtained from ordinary conductance measurements. Here, we present two examples of thermopower measurements on chaotic transport in a quantum dot in two different transport regimes, for the ballistic ($G = 4e^2/h$) and the Coulomb blockade regime (lead conductance $G \leq 2e^2/h$). In both cases the experimental results show an excellent agreement with the theoretical prediction.

1 Introduction

The motion of electrons in very small systems with characteristic sizes much smaller than the electron mean free path can, in fact, be viewed as billiard ball moving in a classically chaotic system where many random reflections at the system boundaries occur. Due to the wave-like nature of electrons, quantum mechanics is needed to describe the system fully. In order to characterize the chaotic behaviour of such quantum mechanical systems, the transport properties of electrostatically defined quantum dots in semiconductor heterostructures have been investigated mainly in the ballistic transport regime [1-3]. The electrical conductance exhibits distinct fluctuations which display correlations as a function of an external parameter such a shape or magnetic field and can be described in a statistical manner. However, the analysis of ordinary conductance measurement turned out to be difficult. So-called short trajectories [4] and weak localization effects [1,5] add up to the signature of chaotic motion. Additionally, current heating effects of the electrons in the quantum dot smear out the underlying chaotic statistics. Therefore, it appeared to be hard to establish experimental evidence for chaos in a quantum mechanic system.

An alternative for the conductance measurements (which inherently are accompanied by electron heating inside the dot) is to investigate the thermoelectric properties of a system. Thermopower measurements have already been used to study semiconductor nanostructures like quantum point-contacts [6] and quantum dots in the Coulomb blockade regime [7]. The thermopower S measures directly the parametric derivative of the conductance, $S \propto G^{-1} \partial G / \partial X$ with $X = E$ (energy), and thus yields both similar and additional information on the electron transport

processes as can be obtained from conductance measurements. The distribution of parametric derivatives ($X = E, B, \text{shape}, \dots$) of the conductance of a quantum dot is the subject of recent random matrix theory (RMT)-investigations [8,9]. The probability distribution for the thermopower and the conductance are expected to be non-Gaussian for chaotic conductors. Additionally, the thermopower probability distribution should exhibit cusps at zero amplitude and non-exponential tails [9,10].

Furthermore, theoretical investigations of chaotic quantum dots predict deviation [11] from the previously predicted power-law scaling of the effective charging energy, E^* , as a function of the coupling leads conductance [12]. Although this result was derived under the assumption that the conductance of the quantum dot leads is close to $2e^2/h$, the predicted scaling behaviour has been experimentally observed so far only for a range of $0 < G < 0.6e^2/h$, using an electrometer device consisting of two coupled quantum dots [13]. In the Coulomb blockade regime the scaling of the effective charging energy is determined from the amplitude and line shape of the thermopower oscillations which depend strongly on the ratio $k_B T/E^*$. For asymmetrical quantum dots, where the classical electron trajectories are chaotic, a residual oscillatory dependence of the transport properties should remain even if the conductance of one of the leads becomes close to $2e^2/h$. This implies a finite effective charging energy for fully transmitting leads which contradicts the linear scaling behaviour. To test the prediction of Ref. [11] a technique is needed that allows for sensitive measurements of the charging energy of a quantum dot even if the transmission probability of a coupling point contact is close to one. According to the theory of Ref. [14], the amplitude and lineshape of the thermopower oscillations depend strongly on the ratio $k_B T/E_c$. Thus measuring the thermovoltage V_{th} of a quantum dot at a fixed temperature for different transmission probabilities of a coupling point contact should provide information about the scaling behaviour of the charging energy.

Here, we present experimental results on the probability distribution of thermopower fluctuations in the ballistic transport regime and scaling behaviour of the charging energy through changes of the amplitude and lineshape of the thermovoltage oscillations in the Coulomb blockade regime of a single chaotic quantum dot.

2 Experiment

The sample, schematically shown in Fig. 1, is electrostatically defined by TiAu Schottky-gates in a two-dimensional electron gas (2DEG) in a GaAs-(Al,Ga)As modulation doped heterostructure. The 2DEG has an electron density $n_s \approx 3.4 \times 10^{11} \text{ cm}^{-2}$ and an electron mobility $\mu \approx 10^6 \text{ cm}^2 (\text{Vs})^{-1}$. The gates define the main features of the sample. The quantum dot with a lithographical size of $700 \times 800 \text{ nm}$ is coupled to the reservoirs by two adjustable barriers forming quantum point-contact (QPC) leads (Q1 and Q2). Next to the quantum dot is a $2 \mu\text{m}$

wide and 20 μm long electron channel with an additional quantum point-contact (Q3) in the channel boundary. Passing a current through this channel any temperature difference can be applied across the quantum dot. QPC Q3 is then used as a reference contact to measure the created thermovoltage. The electrochemical potential and size of the dot can be varied by changing the applied voltage to gate B, V_g , while the tunnel barriers are kept constant. All experiments were done at $T < 40$ mK, using a dilution refrigerator equipped with a superconducting magnet.

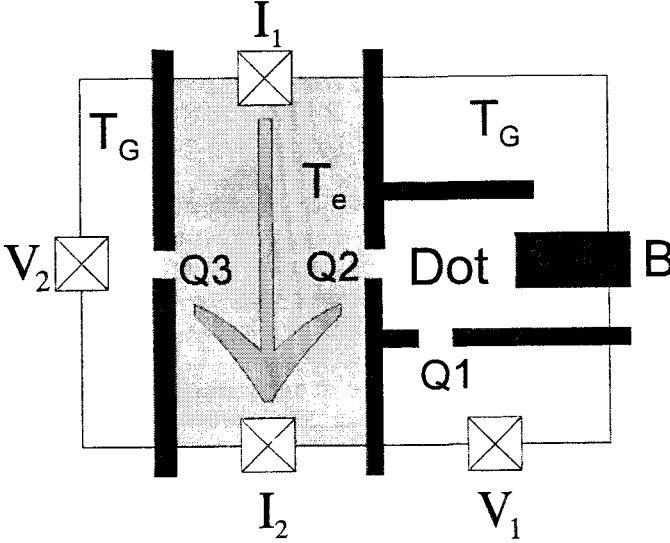


Figure 1. Schematic top view of the sample structure. The black areas show the structure of the Schottky-gates, the crossed squares denote ohmic contacts. The heating current is passed between contacts I_1 and I_2 . The thermovoltage V_{th} is measured between contacts V_1 and V_2 . The dot shape can be varied by controlling the voltage V_g applied to Schottky-gate B.

A temperature difference ΔT across the dot is created by current-heating techniques. A low-frequency (13 Hz) current I is passed through the electron channel, increasing the temperature T_e of the electron system in the channel by $\Delta T \propto I^2$ [6]. Measuring the potential difference between the voltage contacts V_1 and V_2 by phase sensitive lock-in techniques at twice the frequency of the heating current gives a thermovoltage $V_{th} = V_1 - V_2 = (S_{ref} - S_{dot}) / \Delta T$.

Thus, assuming a constant thermopower S_{ref} of the reference quantum point contact Q3 and a constant averaged temperature difference ΔT between the electron channel and the reservoirs, variations of V_{th} reflect directly changes in the thermopower of the dot. The thermopower of the quantum dot was measured as a function of the dot size, magnetic field and transmission probability of the QPC leads.

Standard conductance measurements of this sample reveal the expected strong conductance fluctuations. The left inset of Fig. 2 shows a typical trace for a given dot size as a function of magnetic field. Averaged over a large number of different dot sizes a clear weak-localization peak is observed (right inset Fig. 2). According to RMT-results the width of this peak is directly related to the ratio of dwell time and ergodic time for an electron in the quantum dot [1]. A fit give $\tau_{\text{dwell}} / \tau_{\text{erg}} \approx 5.3$.

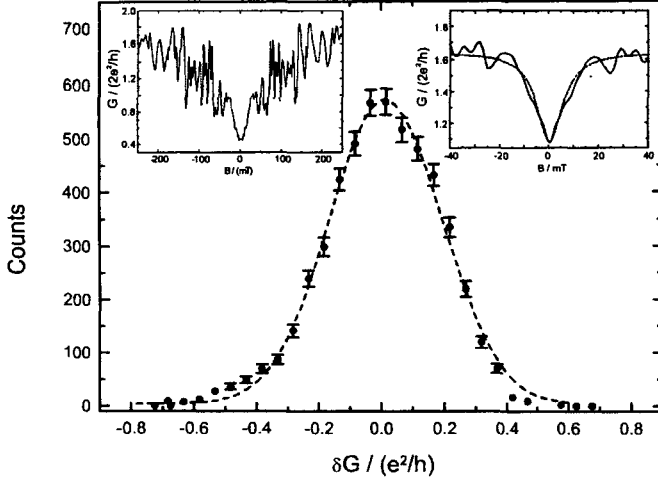


Figure 2. Distribution of conductance fluctuations in a quantum dot. Dashed line is the best Gaussian fit. Left inset shows magnetic field dependent conductance for a fit gate voltage V_g . Right inset shows weak localisation peak for an averaged conductance for different V_g .

Because this ratio is larger than one, the motion of electrons in the dot is inferred to be chaotic. However, the distribution of conductance fluctuations can well be represented by a Gaussian which implies that dephasing obscures the underlying chaotic characteristic of the quantum dot.

3 Thermopower fluctuations

In order to study the statistical distribution of the random fluctuations in the thermopower in the ballistic transport regime conductance of the quantum dot leads was adjusted to $G = 4e^2/h$. To generate a statistic ensemble, we have studied the thermovoltage as a function of dot shape and magnetic field. A very fundamental prediction of quantum chaos theory is that these fluctuations should exhibit a characteristic non-Gaussian distribution. In conductance experiments, such non-Gaussian distributions could not be demonstrated, which is attributed to current

heating effects. In our thermopower experiments, the current is not passed directly through the dot.

A typical trace of the magnetic field dependent thermopower for a fixed dot size is displayed in the left inset of Fig. 3. In the right inset (Fig. 3) the averaged thermopower is shown. From this data, it is directly obvious that weak localization effects are absent in thermopower measurements. Counting the fluctuation amplitudes we obtain the distribution displayed in Fig. 3. Note that in order to compare the experimental data with the theory one has to consider the system symmetry.

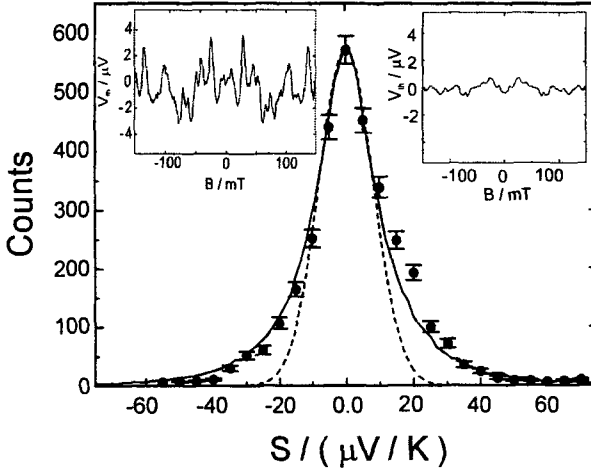


Figure 3. Thermopower fluctuation distribution for broken TRS ($B > 50$ mT). Dashed line is the best Gaussian fit; solid line represents RMT Monte Carlo simulation. Left inset shows magnetic field dependence of the thermovoltage for a fixed gate voltage V_g . Right inset shows averaged thermopower for an static ensemble for various dot sizes.

Time reversal symmetry (TRS) is present for magnetic fields around $B = 0$ and broken for high fields. Therefore, experimental data were split into two regimes: first, TRS is present, $|B| \leq 40$ mT (not shown here), and second, TRS is broken, $|B| \geq 50$ mT. Here, only the case for broken TRS is shown. The situation for TRS is discussed elsewhere [16]. In both cases a strong deviation from a Gaussian distribution (Fig. 3, dotted line) is obtained. Typical are the long tail of the distribution, i.e. a high probability for large thermopower amplitudes is observed. Monte Carlo simulation techniques have been used to calculate the thermopower fluctuation distribution for a quantum dot used in the presented experiments [15]. The resulting simulated distribution is shown as solid lines in Fig. 3. Evidently, the simulations represent the experimental results much better than a Gaussian distribution function. This result is the first direct observation of fluctuations in a transport property that displays an underlying chaotic statistic [16].

4 Charging energy

The chaotic behaviour of the electronic motion in a quantum dot should also effect the charging energy when the conductance of the leads to the dot is changed from the Coulomb-blockade into the ballistic transport regime [11]. The charging energy should approach a constant value $E^* \neq 0$ even if one lead to the quantum dot carries one conducting mode ($G = 2e^2/h$). For a non-chaotic system the charging energy should be zero for $G = 2e^2/h$ [12,13]. The scaling behaviour of the charging energy is determined by measuring V_{th} as a function of V_g for various values of the conductance of Q1. The transmission of Q2 is kept constant at a value of $G \approx 0.06e^2/h$. Some of the resulting curves are shown in the inset of Fig. 4 for a gate-voltage range of $-938 \text{ mV} < V_g < -925 \text{ mV}$. Each thermovoltage oscillation corresponds to a conductance peak (Coulomb-blockade oscillation) [14].

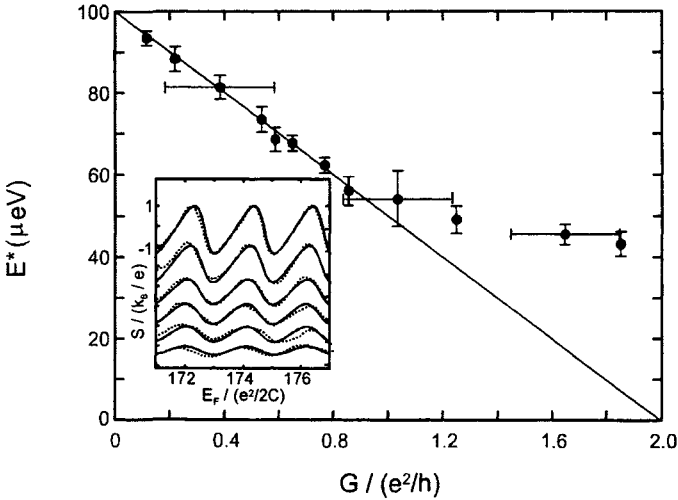


Figure 4. Measured effective charging energy E^* as a function of the conductance of Q1. Solid line shows the expected linear scaling. Inset displays experimental traces of the thermovoltage for a heating current of 40 nA (dotted line). The conductance of Q1 was 0.06, 0.19, 0.29, 0.38, 0.43, and $0.82 \times 2e^2/h$ from top to bottom. Calculated curves of the thermopower of a quantum dot are solid lines. The values of $k_B T/E^*$ are 0.22, 0.25, 0.30, 0.33, 0.37, and 0.45 from top to bottom.

The thermovoltage oscillations decrease with increasing point-contact conductance and become more symmetric.

The experimental curves are fitted using the ratio between thermal energy and charging energy, $k_B T/E^*$ as only variable parameter (dashed lines). Using a bare charging energy of the quantum dot, $E_c \approx 100 \pm 20 \mu\text{eV}$, which was determined from thermal activation studies of the conductance in the Coulomb-blockade regime, it is possible to evaluate the effective charging energy quantitatively.

The dependence of E^* on the conductance of Q1 is displayed in Fig. 4. A remarkable deviation from the expected scaling behaviour for non-chaotic dots (solid line) is observed. The effective charging energy approaches a value of $E^* \approx 0.45 E_0$ for $G \rightarrow 2e^2/h$. Physically, this plateau is caused by electrons that, after being reflected by the closed contact, are not able to find the open contact on the other side of the dot. This chaos-induced effect strongly reduces the charge fluctuations on the dot. Aleiner and Glazman [11] used RMT in connection with the Tomonaga-Luttinger formalism to compute this behaviour. Using this approach E^* can be estimated as $E_c^*(G=2e^2/h) = 0.49 \pm 0.03 E_c$, where a mean level spacing $\Delta E \approx 23 \mu\text{eV}$ is assumed, which was estimated from the 2DEG density of states and the size of the quantum dot. The actual position of the plateau in E^* ($\approx 0.45 E_c$) is in very good agreement with this theoretical predictions [17].

5 Conclusion

We have demonstrated that thermopower measurements help to investigate characteristic properties of chaotic quantum dots. Theoretical predictions on a residual effective charging energy for an asymmetrically adjusted chaotic quantum dots were verified. The expected non-Gaussian distribution of fluctuations in transport related quantities were demonstrated. These experiments reveal thermopower measurement as a powerful tool in investigations of chaotic systems, where conventional transport measurements turn out to have systematic difficulties.

6 Acknowledgments

Part of this work was supported by the Deutsche Forschungsgemeinschaft Grant No. MO 771/3.

References

1. Beenakker C. W. J., *Rev. Mod. Phys.* **69** (1997) 731.
2. Marcus C. M., Rimberg A. J., Westervelt R. M., Hopkins P. F., Gossard A. C., *Phys. Rev. Lett.* **69** (1992) 506.
3. Chan I. H., Clarke R. M., Markus C. M., Campman K., Gossard A. C., *Phys. Rev. Lett.* **74** (1995) 3876.
4. Baranger H. U., Mello P. A., *Europhys. Lett.* **33** (1996) 465.
5. Pluhar Z., Weidenmüller H. A., Zuk J. A., Lewenkopf C. H., *Phys. Rev. Lett.* **73** (1994) 2115; Baranger H. U., Jalabert R. A., Stone A. D., *Phys. Rev. Lett.* **70** (1993) 3876.
6. Molenkamp L. W., van Houten H., Beenakker C. W. J., Eppenga R., Foxon C. T., *Phys. Rev. Lett.* **69** (1990) 731.

7. Molenkamp L. W., Staring A. A. M., Alphenaar B. W., van Houten H., Beenakker C. W. J., *Semicond. Sci. Technol.* **9** (1994) 903; Staring A. A. M., Molenkamp L. W., Alphenaar B. W., van Houten H., Buyk O. J. A., Mabesoone M. A. A., Beenakker C. W. J., Foxon C. T., *Europhys. Lett.* **22** (1993) 57.
8. Fyodorov Y. V., *Phys. Rev. Lett.* **73** (1994) 2688; Fyodorov Y. V.; Mirlin A. D., *Phys. Rev. B* **51** (1995) 13403.
9. Brouwer P. W., van Langen S. A., Frahm K. M., Büttiker M., Beenakker C. W. J., *Phys. Rev. Lett.* **79** (1997) 913.
10. van Langen S. A., Silvestrov P. G., Beenakker C. W. J., *Superlatt. and Microstr.* **23** (1998) 691.
11. Aleiner I. L., Glazman L. I., *Phys. Rev. B* **57** (1998) 9608.
12. Flensberg K., *Phys. Rev. B* **48** (1993) 11156.
13. Molenkamp L. W., Flensberg K., Kemerink M., *Phys. Rev. Lett.* **75** (1995) 4282.
14. Beenakker C. W. J., Staring A. A. M., *Phys. Rev. B* **46** (1992) 9667.
15. Brouwer P. W., van Langen S. A., Frahm K. M., Büttiker M., Beenakker C. W. J., *Phys. Rev. Lett.* **79** (1997) 913.
16. Godijn S. F., Möller S., Buhmann H., Molenkamp L. W., van Langen S. A., *Phys. Rev. Lett.* **82** (1999) 2927.
17. Möller S., Buhmann H., Godijn S. F., Molenkamp L. W., *Phys. Rev. Lett.* **81** (1998) 5197.

POLARONS IN QUANTUM WELLS

A. I. BIBIK¹, M. O. DZERO², B. GERLACH³, M. A. SMONDYREV⁴

¹*Institute of Molecular and Atomic Physics, National Academy of Sciences
F. Skaryna ave. 70, 220072 Minsk, Belarus*

E-mail: bibik@imaph.bas-net.by

²*National High Magnetic Field Laboratory, Florida State University
Tallahassee, Florida 32304, USA*

E-mail: dzero@magnet.fsu.edu

³*Institut für Physik, Universität Dortmund
D-44221 Dortmund, Germany*

E-mail: gerlach@fkt.physik.uni-dortmund.de

⁴*Bogolubov Laboratory of Theoretical Physics
Joint Institute for Nuclear Research
141980 Dubna, Moscow Region, Russia*

E-mail: smond@thsun1.jinr.ru

An approximate model to describe a multilayered heterostructure is proposed. The details of the heterostructure are taken into account by the confining potential $V(z)$ generated by the layers. The multilayered $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ heterostructure is considered as an effective medium. Its mean parameters are defined by averaging the subsequent layer-dependent parameters over the ground-state wave function. Only the effective bulk phonon mode inhabits the effective medium with mean characteristics. As a result, properties of charge carries in the heterostructure can be described through the Pekar-Fröhlich polaron model. The polaron energy and its effective mass are calculated for different quantum wells. We obtained a rather monotonous behavior between the asymptotic values for the polaron energy as a function of the confining potential width. As to the effective polaron mass it exhibits a peak. The comparison is made with theoretical results by other authors.

1 Introduction

Systems with the reduced dimensions - quasi-two dimensional (2D) quantum wells, quasi-one dimensional (1D) quantum wires and quasi-zero dimensional (0D) quantum dots have attracted a lot of attention the last two decades when their practical realization became possible. Now the dominant are investigations of semiconductor heterostructures instead of bulk samples. The opportunity to

engineer electronic properties of a device “as desired” made these systems advantageous both for basic research and technical applications.

The first layered heterostructures were created at early seventies, and we give in [1] the compilation of some literature. One of the most common heterostructures is the so called quantum well where a layer of some material is sandwiched between two layers of another material. If the thickness of the inner layer (typically in the range of 10-1000 Å) is much smaller than the thickness of the outer layers, the latter can be considered as half-space bulk samples. The difference in the band gaps in the materials of the well and of the barrier causes a band-edge profile depending on the coordinate of the layer growth which acts on the particles like a potential. The order of magnitude of the energetic barriers is typically about a few hundreds meV. Due to the fascinating technological progress in the field of artificial structures, it has become possible to fabricate quantum wells and wires of a widely varying shape. We reproduce samples in Figs. 1-3.

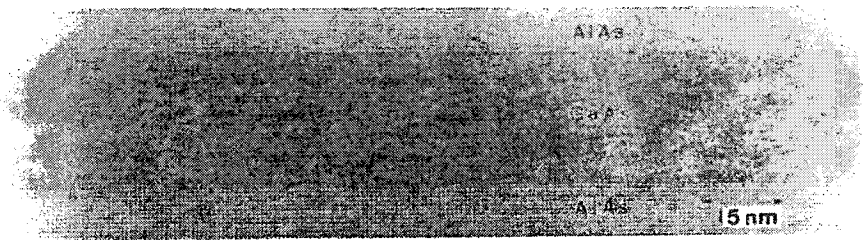


Figure 1. The high resolution TEM image of the 8 nm GaAs layer (a quantum well) inside an AlAs medium (a barrier) of the sample with 100 s interruption of growth at both interfaces (by courtesy of Dr. W. Langbein, Dortmund University).

The purpose of this contribution is to analyze the dependence of the energy of an elementary excitation on the width of the confinement potential, which exists in a planar semiconductor heterostructure. Concerning the excitations of interest, we concentrate on electron-phonon systems. The simplest example is an electron coupled to a certain branch of lattice vibrations. This has direct implications for the transport behavior of the materials of interest. The tiny structures under discussion reveal many new features to be studied. In particular, if a heterostructure is made of polar materials such as GaAs, InAs, etc., the electron-phonon interaction modifies properties of the electron confined to a quantum well (wire, dot). The electron surrounded by the cloud of virtual phonons becomes a quasi-particle - the polaron. This results in shifting of its binding energy and the effective band mass. Naturally, these changes depend on the confining potential. It is an interesting theoretical task to discuss the excitation spectrum of such semiconductor structures as function of the tunable parameters, such as well width, well height, etc.

To demonstrate what we can face with let us consider qualitatively a Coulomb potential localized in the center of a quasi-two dimensional heterostructure of the

width L . Imagine at first that the confining potential is infinitely high. Then at large L we deal with the conventional three-dimensional Coulomb potential $\propto 1/r$ with the binding energy which is equal exactly to the Rydberg energy: $E(\infty) = 1Ry$. At small width the corresponding energy is known to be equal to four Rydbergs: $E(0) = 4Ry$ (this is the exact solution for the two-dimensional Coulomb potential $\propto 1/\rho$). Then, the curve $E(L)$ decreases monotonously from $4Ry$ to $1Ry$ with increasing L .

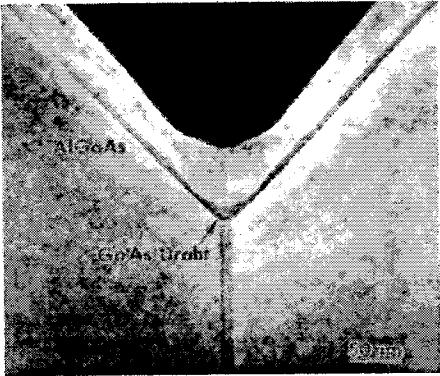


Figure 2. A quantum wire made of GaAs (Forschungszentrum Jülich, Germany; <http://www.nanonet.de>).

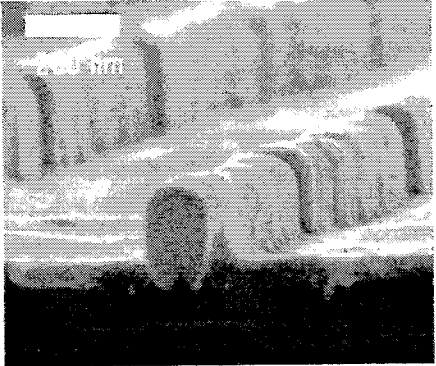


Figure 3. Replicated nanostructures (Laboratory for Micro- and Nanotechnology, PSI, Villigen, Switzerland; http://www1.psi.ch/www_lmn_hn/).

Consider now the same procedure for the quantum well of a finite height. The behavior of $E(L)$ should be the same at large L because the finiteness of the potential does not affect the particle state. But at the small potential width, when the ground-state energy level approaches the edge of the potential, the wave function is spread over the barrier, and due to tunnelling the limiting value for the energy will be equal again to the three-dimensional limit. That is, $E(0) = E(\infty) = 1Ry$, and the energy $E(L)$ has a maximum at some intermediate value of the width L .

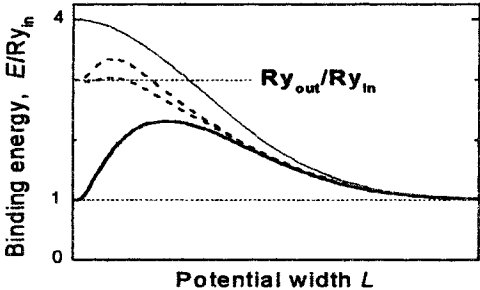


Figure 4. A naive picture for the energy dependence on the confining potential width for the infinitely high well (thin curve), finite potential when materials of the well and the barrier are the same (solid curve) and possible alternatives for the real case when Rydberg energies are different for the well and the barrier (dashed curves).

We assumed here that the quantum well and the barrier are made of the same material. If not (what is the general case) then we have the two Rydberg energies: Ry_{in} for the material of the well and Ry_{out} for the material of the barrier (usually $Ry_{out} > Ry_{in}$). The question then arises if the peak of the function $E(L)$ will survive in these conditions? The same question is to be answered concerning the behavior of the polaron effective mass. The above discussion is illustrated in Fig. 4.

2 Background and formulation of the model

The physics of polarons confined to quantum wells passed a few stages which we can classify as follows.

a) At earlier stages the attention was paid to the properties of a polaron confined to an infinite thin 2D layer [2-4], i.e. the confining potential was assumed to have zero width and infinite height. In particular, the result for the polaron self-energy was found to be $\Delta_2 E^{(2D)} = \alpha_{in} \hbar \omega_{in} \pi / 2$ and the shift of the polaron effective mass $\Delta_2 m^{(2D)} = m_{in} \alpha_{in} \pi / 8$. Here m_{in} is the electron band mass which is related to the quantum well material (as well as the parameters α_{in} is the standard Fröhlich electron-phonon coupling constant, and ω_{in} is the LO-phonons frequency. Let us remind the subsequent results for the 3D polaron: $\Delta_2 E^{(3D)} = \alpha_{in} \hbar \omega_{in}$ and $\Delta_2 m^{(3D)} = m_{in} \alpha_{in} / 6$.

b) Then the binding energy and the effective mass were calculated in [5,6] for an infinitely deep quantum well of a finite width. The behavior of the polaron energy and the effective mass between their 2D- and 3D-limits is similar to the thin solid curve in Fig. 4.

c) Only the interaction with the bulk LO-phonon mode has been taken into account in the cited papers. Actually, this mode is modified in a 2D layer and becomes the so called confined slab mode. Besides, there appear an interface optical-phonon mode and a half-space phonon mode in a barrier material [7-14]. The influence of the mentioned phonon modes on polarons were studied in [15-18].

d) Finally, the authors of the papers [19,20] considered finite rectangular wells (one layer heterostructure) taking into account contributions of all LO-phonon modes.

Anyway, there are still problems to be addressed while dealing with multilayered heterostructures. Namely, we have to answer the following questions:

- How to deal with multilayered heterostructures? The number of phonon modes becomes too large to make numerical calculations even with modern computers. Besides, a multilayered heterostructure can generate a confining potential of rather complicated form, not only the rectangular one.
- How to deal with mass- and dielectric mismatches in different layers? The electron band mass, the electron-phonon coupling constant, and the phonon

dispersion law do depend on a layer, that is, on the electron position. To match the solutions in different layers seems to be a cumbersome job.

To tackle these problems we suggest specific approximations which will be briefly indicated here. We consider a quantum well in the z direction constructed of the xy plane layers of $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$. That is, the Al mole fraction x depends on the coordinate z , and so the other parameters - the electron band mass $m(z)$, the LO-phonon frequency $\omega(z)$ and the electron-phonon coupling constant $\alpha(z)$. The confining potential $V(z)$ generated by the energy gaps of different layers is taken into account explicitly being considered as the main entity of the model. This heterostructure is considered as an effective medium. Its mean parameters are to be defined by averaging over different layers according to the way they enter the Hamiltonian. The bulk phonon mode only inhabits an effective medium.

Thus, we specify the electronic part of the Hamiltonian:

$$H_{\text{el}} = H_{\text{el},\parallel} + H_{\text{el},\perp},$$

$$H_{\text{el},\parallel} = \frac{p_{\parallel}^2}{2m}, \quad H_{\text{el},\perp} = \frac{p_{\perp}^2}{2m} + V(z)$$

where the electron mean band mass m is defined by the relation:

$$\frac{1}{m} = \int dz \frac{|\Psi_1(z)|^2}{m(z)},$$

and the ground-state wave function for the electron motion in z direction satisfies the Schrödinger equation: $H_{\text{el},\perp}\Psi_1 = E_1\Psi_1$. As the wave function Ψ_1 also depends on m , our definition of the latter together with the Schrödinger equation become a system of two equations to be solved.

In a similar way we define the mean phonon frequency ω_{LO} in the phononic part of the total Hamiltonian and the mean electron-phonon coupling constant α in the interaction term. For the details we refer to our publication [21] where the dependence of the medium parameters on the Al mole fraction x is also presented (which is taken with some modifications from the paper [22]). Evidently, all mean parameters m , ω_{LO} and α do depend on the width L of the confining potential.

For the rectangular potentials we derived an internal validity criterion of the model. Namely, we compare the width L^{av} when a first excited level appears in our model with the exact solution L^{ex} for the symmetrical rectangular potential and found:

$$\frac{L^{\text{av}}}{L^{\text{ex}}} = \sqrt{0.844 + 0.156 \frac{m_{\text{in}}}{m_{\text{out}}}},$$

where $m_{\text{in(out)}}$ are electron band masses inside the well and in the barrier material. At the Al mole fraction $x = 0.3$ we obtained $L^{\text{av}} = 48.6 \text{ \AA}$ and $L^{\text{ex}} = 49.6 \text{ \AA}$, so that the relative discrepancy $\delta L \approx 2 \%$.

3 Results and discussion

We applied our model to the following confining potentials.

(i) Rectangular confining potential:

$$V(z) = \begin{cases} 0, & |z| < L/2, \\ V_0, & |z| \geq L/2. \end{cases}$$

This potential was studied in [19,20], but the authors used different parametrizations of the experimental data, so their results cannot be compared directly. The potential depth is given as $V_0 = 227.9$ meV at the Al mole concentration $x = 0.3$ in the parametrization [19] and $V_0 = 199.6$ meV at $x = 0.25$ in the parametrization [20]. These values we use in what follows.

It is possible however to compare the results of [19,20] with our model. The energy shift $\Delta_2 E$ and the ratio of the effective polaron mass shift to the shift in GaAs $\delta_2 m = \Delta_2 m / \Delta_2 m_{in}$ are presented in Fig. 5. As we see, the comparison with [19]

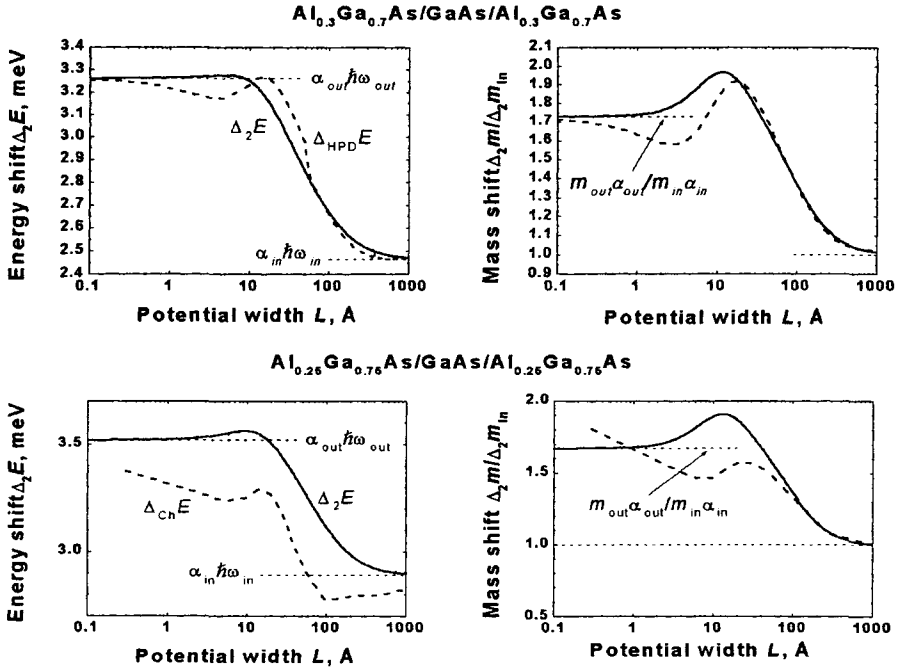


Figure 5. A comparison of our results [21] (solid curves) with those of Ref. [19] (upper plots, dashed curves) and Ref. [20] (lower plots, dashed curves) for the polaron energy (left plots) and the effective mass (right plots) in the symmetrical rectangular potentials.

is quite satisfactory: the results for the energy at $L \geq 50$ Å and for the mass at $L \geq 20$ Å are practically the same. Our model does not reproduce the more complicated structure with the peak and the dip which appears because of the presence of several phonon modes. But the difference between the peak and the dip found in [19] is about 0.1 meV (3 %) which is within the accuracy of our model and hardly can be seen experimentally. The discrepancy with the results of [20] is more crucial, and we have to conclude that something is wrong in that paper. For instance, the curve for the energy shift evidently should approach its asymptotic at large potential width from the other side in comparison with $\Delta_{ch}E$ in Fig. 5.

(ii) Asymmetrical rectangular potential:

$$V(z) = \begin{cases} V_l, & z \leq -L/2, \\ 0, & |z| < L/2, \\ V_r, & z \geq L/2. \end{cases}$$

As an example we use the following values for the Al mole fractions: $x_l = 0.42$ ($V_l = 346.6$ meV) to the left from the quantum well and $x_r = 0.18$ ($V_r = 141.8$ meV) to the right of it.

In Fig. 6 we present our calculations for the asymmetrical rectangular potential. The contributions are from the discrete spectrum (lower index *dis*) and the parts of continuous spectrum with energies $V_r \leq E \leq V_l$ (lower index *con, V*) and $E \geq V_l$ (lower index *con, ∞*). The main peculiarity in comparison with the symmetrical rectangular well is that the ground-state level stops to exist at small enough width of the well (about 16 Å in our case). Again we notice large discrepancies with the results of [20].

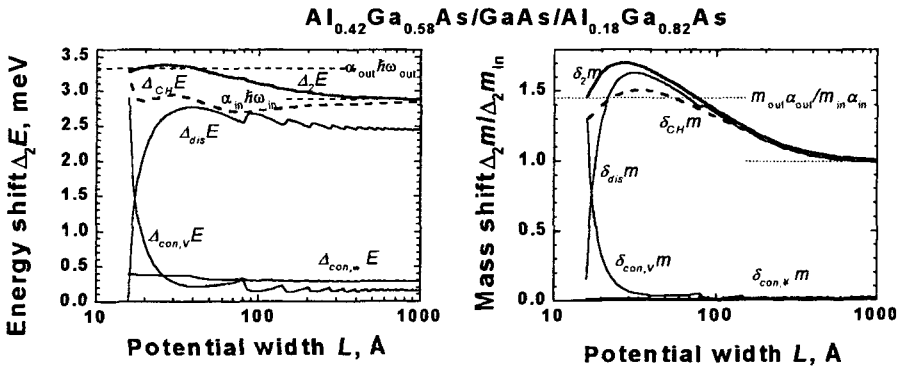


Figure 6. A comparison of our results [23] (solid curves $\Delta_2 E, \delta_2 m$) with those of [20] (dashed curves $\Delta_{CH} E, \delta_{CH} m$) for the polaron energy (left plot) and the effective mass (right plot) in the asymmetrical rectangular potential.

(iii) Rosen-Morse potential:

$$V(z) = V_0 \tanh^2 \frac{z}{L_{RM}}.$$

In both previous cases the mathematical method used was the perturbation theory in powers of α . For the Rosen-Morse potential instead of the direct summation over all virtual states we use the energy-dependent Green function which is known explicitly for this potential [24,25]. Then the Rosen-Morse potential serves as an example of a multilayered heterostructure. It is used also as a tool to check the model. There is a link between the parameter L_{RM} and the width of an equivalent rectangular potential which allows to compare both results. The coincidence is perfect [21] which verifies the technical part of our calculations.

4 Conclusions

We suggested a model which describes a multilayered GaAs/Al_xGa_{1-x}As heterostructure as an effective medium with one (bulk) phonon mode. The polaron energy and effective mass were calculated for different Al mole fractions. Peaks were found for the effective mass at some potential widths while the energy demonstrates rather smooth behavior between the correct 3D-limits. Hunting of the peaks can be extended to other similar systems: bound polarons, D-centers, bipolarons, etc. confined to a quasi-2D quantum wells. The methods developed can be applied as well to quantum wires and quantum dots.

5 Acknowledgments

The support of the Heisenberg-Landau program is gratefully acknowledged. A. B. thanks the Joint Institute for Nuclear Research for the possibility to visit Dubna. We are grateful to the organizers of the „Nanomeeting ‘2001“ for the kind invitation.

References

1. Esaki L., Tsui T., *IBM J. Res. Dev.* **14** (1970) 61; Bauer G., Kucher F., Heinrich H., *Two-dimensional systems, heterostructures and superlattices* (Springer, 1984); Chang L. L., Ploog K., *MBE and heterostructures* (Nijhoff, 1985); Casey H. C., Panish M. B., *Heterostructure Lasers* (Ac. Press, 1978); Woggon U., Gaponenko S. V., *Phys. Stat. Sol. B* **189** (1995) 285; D'Andrea A., Del Sole R., Girlanda R., Quattropani A., *Optics of Excitons in confined systems* (Institute of Phys. Conference Series No. 123, 1991).
2. Das Sarma S., Mason B. A., *Ann. Phys.* **163** (1985) 78.
3. Peeters F. M., Wu X., Devreese J. T., *Phys. Rev. B* **31** (1985) 3420; *Phys. Rev. B* **33** (1986) 3926.

4. Seljugin O. V., Smondyrev M. A., *Physica A* **142** (1987) 555.
5. Das Sarma S., *Phys. Rev. B* **27** (1983) 2590.
6. Das Sarma S., Stopa M. *Phys. Rev. B* **36** (1987) 9595.
7. Bryksin V. V., Firsov Yu. A., *Fiz. Tverd. Tela* **13** (1971) 496, [*Sov. Phys. Solid State* **13** (1971) 398].
8. Licari J. J., Evrard R., *Phys. Rev. B* **15** (1977) 2254.
9. Fomin V. M., Pokatilov E. P., *Phys. Stat. Sol. (b)* **132** (1985) 69.
10. Wendler L., Pechstedt R., *Phys. Stat. Sol. (b)* **138** (1986) 196; *Phys. Stat. Sol. (b)* **141** (1987) 129
11. Wendler L., Haupt R., *Phys. Stat. Sol. (b)* **143** (1987) 487.
12. Pokatilov E. P., Fomin V. M., Beril S. I.; *Vibrational excitations, polarons and excitons in multi-layer systems and superlattices* (Shtiintsa, Kishinev, 1990) (in Russian).
13. Fomin V. M., Pokatilov E. P. In *Formation of Semiconductor Interfaces*, Proc. of the 4th International Conference. Forschungszentrum Jülich, (World Scientific, Singapore, 1994) pp. 704-707.
14. Klimin S. N., Pokatilov E. P., Fomin V. M., *Phys. Stat. Sol. B* **190** (1995) 441.
15. Licari J. J., *Solid State Commun.* **29** (1979) 625.
16. Liang X. X., Gu S. W., Lin D. L., *Phys. Rev. B* **34** (1986) 2807.
17. Cosmas F., Trallero-Giner C., Riera R., *Phys. Rev. B* **39** (1989) 5907.
18. Degani M. H., Hipólito O., *Phys. Rev. B* **35** (1989) 7717.
19. Hai G. Q., Peeters F. M., Devreese J. T., *Phys. Rev. B* **48** (1993) 4666; Erratum. *Phys. Rev. B* **62** (2000) 10572.
20. Shi J. J., Zhu X. Q., Liu Z. X., Pan S. H., Li X. Y., *Phys. Rev. B* **55** (1997) 4670.
21. Smondyrev M. A., Gerlach B., Dzero M. O., *Phys. Rev. B* **62** (2000) 16692.
22. Adachi S., *J. Appl. Phys.* **58** (1985) R1.
23. Bibik A. I., Gerlach B., Smondyrev M. A. (unpublished).
24. Kleinert H., Mustapic I., *J. Math. Phys.* **33** (1992) 643.
25. Fischer W., Leschke H., Müller P. In *Path Integrals from meV to MeV: Tutzing '92*, ed. by Grabert H., Inomata A., Schulman L. S., Weiss U. (World Scientific, Singapore, 1993), p. 259; *Ann. Phys.* **227** (1993) 206.

INVITED

SELF-ASSEMBLING SiGe DOTS: NUCLEATION AND GROWTH

I. BERBEZIER, A. PORTAVOCE, F. VOLPI, A. RONDA

*C.R.M.C.2 - C.N.R.S. Campus de Luminy
Case 913, 13288 Marseille CEDEX 9*

E-mail: berbezier@crmc2.univ-mrs.fr

This paper presents a comprehensive review on the fabrication and properties of germanium based nanostructures formed by self-assembling process. The 2D - 3D transition is described in detail. The influence of the Si substrate orientation on the $\text{Si}_{1-x}\text{Ge}_x$ growth modes and relaxation mechanisms is also discussed. We show that while island formation can be described by the classic S-K growth scheme on Si(111), more complex mechanisms based on the competitive effects of kinetics and thermodynamics take place on (001). In the latter case, we define four main growth regimes that are driven either by kinetic growth instability or by stress relaxation and that correspond to four different steady state morphologies (obtained after long term annealing of the as grown samples). These steady state equilibrium morphologies consist of: rough 2D layer in regime I, strained "hut" (105) faceted islands in regime II, coexistence of "hut" and "dome" in regime III and bimodal size distribution of relaxed (elastic or plastic relaxation) "domes" in regime IV.

1 Introduction

Since beginning of the seventies, the microelectronics industry has followed an exponential progress based on scaling down silicon transistors. The International Technology Roadmap for Semiconductors [1] has predicted that this evolution will continue for the next 15 years reaching mass production of circuits with density up to 180 millions transistors per cm^2 (based on scaling down technology up to ~ 35 nm). However, even if future technological progresses can lead to improved performances (both in nanolithography and in device and/or circuit design) alternative routes to CMOS technology should definitively be developed for features sizes approaching 30 nm, mostly because of the problems of self-heating due to power dissipation in logic circuits and of scaling down the storage capacitors in DRAM cells [2]. New generation of nanometric nonvolatile semiconductor memories (NVSM) should then be found before this deadline to permit current scaling trend to continue after the conventional DRAM approach.

The bipolar transistor was the technology driver at the beginning of the modern electronic era (1950-1970), from 1970 to 1990, the DRAM and microprocessor were the technology drivers and since 1990, NVSM has become the technology driver [3]. A key member of the NVSM family is the flash memory, which has captured about 70 % of the NVSM market. Nanocrystal memories belong to this

class of memories and present the advantage to be experimentally feasible at present. Moreover, even if market characteristics are quite different in Si and in III-V devices, since the former evolves towards integration engineering and the latter towards bandgap engineering. In integration engineering, advanced technology is driven by commercial DRAM and NVSM circuitry. In bandgap engineering, basic physics and sophistication of epitaxial technology are key points, spanning the entire range from basic device concepts to commercial devices. It is interesting that some of the advanced research in Si and III-V devices is converging simultaneously towards quantum dot systems [4]. While it would be premature to conclude that future information processing will be based on quantum computing, it is certain that the smallest devices will be affected by quantum confinement and other quantum effects.

In this context nanocrystal memories in particular (which can be integrated in logic circuit to form a system on a chip) but also all the quantum devices (that could serve for opto- and nanoelectronics applications), have great prospects to meet the future technological challenges. Considering now the nanocrystal memories scheme [5,6] it utilizes a new concept based on a highly charged sensitive one transistor floating-dot memory-cell. In this kind of memory structure, the floating gate is constituted of nanocrystals embedded in an oxide layer. One of the major bottlenecks of these emerging devices relies on the lack of reproducibility of nanocrystals (in particular the heterogeneity of their size and shape and the random distribution). Two main approaches of fabrication are investigated at present: implantation of silicon nanocrystals into the oxide layer [7,8] and growth of self-organised Ge quantum dots (QDs) on Si [9]. The latter system presents some advantages as compared to implantation process: (1) a much larger confinement energy (if Ge QDs could be embedded in a SiO_2 layer by a post -growth process), (2) a better lateral organisation of dots and (3) a confinement achievable more easily in practice (i.e. Ge QDs sizes can be larger).

It is consequently a key issue to clarify whether self-assembling of Ge QDs could create sufficiently dense arrays of QDs with high aspect ratio (height over lateral dimension), small lateral sizes and uniform diameters and spacing. Since the formation of islands is governed by a competition between kinetics and thermodynamics, it is of crucial importance to understand the nucleation/growth mechanism of QDs in order to improve the size and shape homogeneity and the lateral arrangement as well.

It is commonly reported that self-assembling of QDs goes through the classical stages of nucleation and growth of islands followed by a last sequence of coarsening (Oswald ripening or other diffusive mechanism) [10]. The deposition of pure Ge on Si is commonly described as a classic Stranski-Krastanov (SK) process. It has been recently shown that the growth on (001) is considerably more complex than the simplified SK growth scheme observed on (111). Briefly, Ge deposition on (001) can be summarized as follows [11-14]: at the first stage, growth proceeds in a layer by layer mode characterised by a fast increase of the ML step density and the

formation of dimer vacancies that order in a $(2 \times n)$ reconstruction. 3D islands start to form just after this surface roughening, probably using the micro-roughness as nucleation centres [15]. As coverage continues to increase, different temperature dependent metastable morphologies occur (hut clusters, domes ...), that finally undergo a phase transition towards very large ($\phi \geq 1 \mu\text{m}$) dislocated islands [16]. However, in this scheme of growth, the origin of the first stage of roughening is still under debate (kinetic or stress driven instability). Also, the origin of the formation of hut islands and the transition from huts to domes are a matter of controversy. Finally, usual models do not consider the role of orientation and atomic configuration of substrates (surface diffusion anisotropy for instance) on the shape of the deposited layers.

This review summarizes the current status of research in the field of nucleation, growth and organisation of $\text{Si}_{1-x}\text{Ge}_x$ QDs. Particular attention is paid to the comparison of the $\text{Si}_{1-x}\text{Ge}_x$ surface evolution on $\text{Si}(111)$ and on $\text{Si}(001)$. In particular we report a systematic investigation of $\text{Si}_{1-x}\text{Ge}_x$ island morphologies that form in between the 2D-3D growth transition (with the exception of dislocated-induced morphologies). We show that 4 growth regimes can be distinguished on (001) and only two on (111): on (001) kinetic undulations form in the low misfit regime, and well separated islands of different shapes form in the higher misfit regime [17]. Such metastable strained morphologies are completely inhibited when $\text{Si}_{1-x}\text{Ge}_x$ layers are deposited on $\text{Si}(111)$ [18]. Finally we show the role of elastic relaxation on the onset of island shapes on $\text{Si}(001)$. In particular, relaxation levels of $\sim 0.2\%$ and $\sim 0.8\%$ of the initial stress (slight variations are also found as a function of the misfit) are attributed to huts and domes respectively [19].

2 Experimental

$\text{Si}_{1-x}\text{Ge}_x$ layers were grown in a Riber molecular beam epitaxy (MBE) system with a base pressure of $\sim 10^{-11}$ Torr. Si and Ge were deposited from an electron beam evaporator and an effusion Knudsen cell, respectively. Si/Ge flux ratios were adjusted to obtain $\text{Si}_{1-x}\text{Ge}_x$ with x comprised between 0.1 and 1. Deposition rate of Si was maintained about 0.03 nm/s. The growth temperature was 550 °C.

Low resistivity nominally singular Si wafers were chemically cleaned ex-situ and protected with an oxide cap layer during the final step. Subsequent in-situ cleaning consisted of thermal desorption of the oxide layer at temperature about 900 °C. A 50 nm thick Si buffer layer was systematically grown to achieve reproducible surface whose cleanliness is qualitatively checked by the reflection high energy electron diffraction (RHEED) intensity of the reconstruction streaks. In situ control of the growth mode and stress relaxation is achieved by using real time acquisition of RHEED patterns along $\langle 110 \rangle$ azimuth.

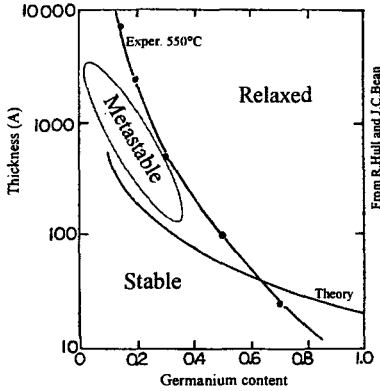


Figure 1. Schematic view of strained, metastable and relaxed states of $\text{Si}_{1-x}\text{Ge}_x$ alloys as a function of thickness and concentration of Ge.

3 Results

Although there exist extensive theoretical and experimental studies on the strain relaxation mechanisms [20-30], the role of substrate orientation has been poorly investigated [31-33]. To date, most of the works concerning strain relaxation is focused on heterostructures grown on Si(001) which is the dominant orientation used for device applications. The growth instability usually observed on Si(001) is explained by the pioneering model of Asaro-Tiller [34] revised by Grinfeld [35] (referred hereafter ATG model). Following the classical concepts, at low misfits, the thin planar epitaxial layer is expected to be coherent with the thick Si substrate. The strain of the epilayer lattice is described by the standard linear elasticity theory (Hooke's law):

$$\sigma_{ij} = [C] \epsilon_{kl}, \quad (1)$$

where σ_{ij} and ϵ_{kl} are the stress and strain tensors, respectively, and $[C]$ is the elastic constants matrix.

For the growth of $\text{Si}_{1-x}\text{Ge}_x$ on Si(100), the film is biaxially compressed in the growth plane and expands in the direction perpendicular to it. Therefore, $\epsilon_1 = \epsilon_2 = -m$, where m is the misfit defined by $(a_{\text{SiGe}} - a_{\text{Si}})/a_{\text{Si}}$ with a_{SiGe} and a_{Si} the $\text{Si}_{1-x}\text{Ge}_x$ and Si lattice parameters respectively. ϵ_3 is the tetragonal distortion of the layer (ϵ_L). For the growth on Si(001), ϵ_L is described by:

$$\epsilon_L = (-2\nu) m / (1 - \nu) = -2 m C_{12}/C_{11}, \quad (2)$$

where ν is Poisson's ratio and C_{ij} are the appropriate elastic constants of the $\text{Si}_{1-x}\text{Ge}_x$ alloy.

The $\text{Si}_{1-x}\text{Ge}_x$ deposited thickness was adjusted to maintain the structures in metastable states (see Fig. 1), just below the critical thickness of dislocation nucleation (h_{cr}) but higher than the theoretical critical thickness for islanding (H_{cr}). Morphological characterization was performed by atomic force microscopy (AFM) in air in non contact mode.

Lateral elastic relaxation ($\Delta\epsilon_{xx}$) was deduced from the measurement of the (220) bulk peak diffraction obtained by grazing incidence X-ray diffraction (GIXRD). Structural characterization was performed by transmission electron microscopy (TEM) cross-section and plane-view analyses in a conventional 200 kV microscope.

For the growth on (111), the film is anisotropically compressed along $\langle 110 \rangle$ and $\langle 112 \rangle$. The elastic and shear moduli and the Poisson's ratio must be decomposed along these two directions. The tetragonal distortion is then described by:

$$\varepsilon_{\perp} = 2m [(C_{11} + 2C_{12}) - 2C_{44}] / [(C_{11} + 2C_{12}) + 4C_{44}]. \quad (3)$$

Regarding these expressions, a tetragonal distortion 1.8 times larger is expected on Si(001) than on (111). Moreover, the elastic energy stored inside the layer (E_{el}) given by:

$$E_{el} = 2\mu m^2 (1 + \nu)/(1 - \nu) \text{ (GPa)}, \quad (4)$$

is about 20 % lower on (001) than on (111). For instance at $m = 1.2\%$ ($x = 0.3$), $E_{el} = 0.024$ GPa and $E_{el} = 0.031$ GPa on (001) and (111), respectively.

This difference is important in the framework of the Asaro ATG instability modelling where the instability was shown to develop when the elastic energy reduction (ΔE_{el}) due to the strain release at step edges is larger than the additional surface energy (ΔF), i.e. when :

$$\Delta E = \Delta E_{el} + \Delta F < 0. \quad (5)$$

The additional surface free energy ΔF in (5) associated with the corrugation has mainly two components, which are the surface energy and the step energy that are both identical for Si(111) and (001) [36]. Consequently, the ATG instability is assumed to rely on ΔE_{el} which is proportional to E_{el} [29]. Considering the results of the calculations (4), ΔE_{el} should be 20 % lower on (001) than on (111) and the ATG instability should develop at higher critical thickness H_{cr} (and/or critical misfit) on Si(001) than on (111). Thus, in the low misfit range, the elasticity theory shows that: (i) a higher tetragonal distortion and (ii) a higher critical thickness H_{cr} and/or critical misfit for ATG development are expected on (001) than on (111).

Considering now plastic relaxation mechanisms (corresponding to nucleation of dislocation) that have been the subject of extensive work [37-43] the authors generally define a critical thickness (h_{cr}) at which it is energetically favourable to relax the elastic strain by introducing misfit dislocations in the heteroepitaxial thin film. The h_{cr} calculation [44,45] is based on an energetic balance between the elastic energy per unit area of a biaxially stressed coherent film and the dislocation energy per unit area of an incoherent film. We have calculated h_{cr} with the well known expression of Matthews *et al.* [46], for a 90° Shockley partial $a/6 \langle 112 \rangle$ dislocation on Si(111) and for an undissociated $a/2 \langle 110 \rangle$ dislocation on Si(100) that were both experimentally evidenced by HREM analyses [37]. Such calculations evidenced a slightly lower h_{cr} on Si(001) than on (111) [47].

Regarding the classical concepts recalled above on the onset of the ATG instability and on the relaxation by misfit dislocation, about similar $\text{Si}_{1-x}\text{Ge}_x$ growth modes could be expected on (001) and (111).

In practice, even if the critical thickness for stress relaxation is the same on both orientations [17,48], huge differences are found in the 2D-3D growth transition. In particular, the island formation and evolution are very different on (001) and (111), the (001) being unique for the formation of metastable coherent

(dislocation-free) islands. In fact, all the metastable states observed on (001) are completely inhibited on (111), as we reported in [49]. To summarize the behavior on both orientations, kinetic phase diagrams of surface morphologies as a function of the two most relevant parameters (the deposited thickness h and the misfit ϵ) are presented in Fig. 2. They have been extracted from systematic investigations of as-grown $\text{Si}_{1-x}\text{Ge}_x$ surfaces that occurred, in our growth conditions, by a competition between kinetics (step flow growth and very high supersaturation) and thermodynamics processes.

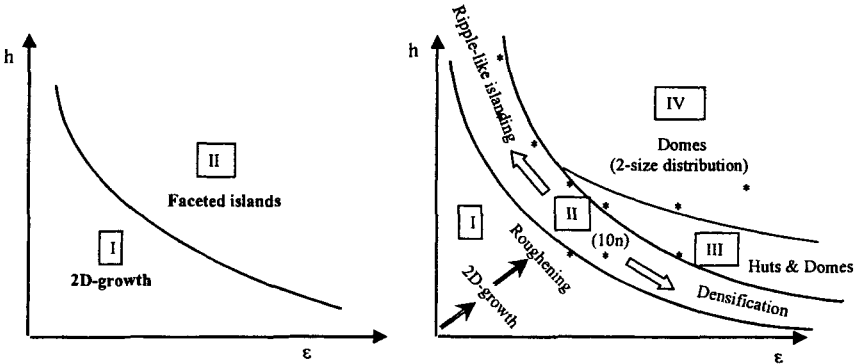


Figure 2. Kinetic phase diagram (at growth temperature $\sim 550^\circ\text{C}$) representing the main growth regimes as a function of the deposited thickness (h) and the misfit (ϵ) on (a) Si(111) and (b) Si(001).

On Si(111) only two growth regimes can be distinguished: 2D layer by layer growth at low (h , ϵ) and classical SK growth at high (h , ϵ). In the latter case plastically relaxed islands that present large facets oriented along (113) and (111) have been obtained. Undulations and dislocation-free islands were never observed on this substrate orientation. On (001) the evolution of $\text{Si}_{1-x}\text{Ge}_x$ surfaces is quite different and can be broken into four main regimes.

Regime I is characterized by a layer by layer growth accompanied by a gradual increase of surface roughness which primarily consists of dimer vacancies [50], kinks and additional steps [51,52]. Vacancies are assumed to serve as a strain-relief mechanism [10,14]. At sufficiently high density of vacancies they order to form the $(2\times n)$ reconstruction which presumably further reduces the strain energy. Even if surface roughness increases very rapidly in this regime, the steady state morphology is characterized by succession of S_A and S_B steps oriented along $\langle 110 \rangle$. A comprehensive review on quantitative scanning tunneling microscopy (STM) analysis of surface roughening during submonolayer growth of Ge on Si(001) can be found in [14].

In *regime II*, ripplelike islands (or undulations) that exhibit a broad distribution in size and in shape are observed at low h and ϵ . The striking feature of these ripplelike islands is their side orientation along $\langle 100 \rangle$ directions. Furthermore at increasing thickness they elongate in chains or in square patterns oriented along

[100] and [010] as it is illustrated in Fig. 3. They present very small aspect ratios ($h/L \sim 0.03$) and side angles about $\sim 5^\circ$ (instead of 11.3° for (105) facets) without extended facet on their sides.

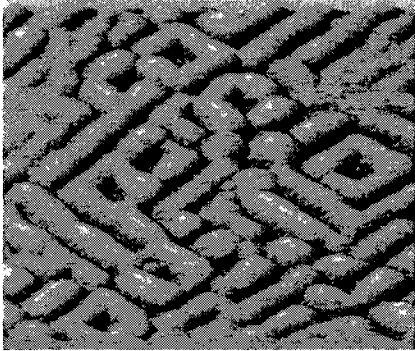


Figure 3. AFM image of ripple-like islands elongated along $\langle 100 \rangle$ and $\langle 010 \rangle$ directions obtained in *regime I* for $\text{Si}_{0.85}\text{Ge}_{0.15}$ ($h = 100$ nm).

Previous results have shown that such undulations are fully strained [17] (since $\Delta\epsilon_{xx} \sim 0$ was found by both convergent beam electron diffraction (CBED) and grazing incidence X-ray diffraction (GIXRD)). The kinetics of ripplelike island formation along the $\langle 100 \rangle$ directions i.e. at 45° from the $(2\times n)$ reconstruction rows is still unclear. It turns out that such morphologies can be equilibrium structures of (001) surface subjected to biaxial compressive stress [52,53] but it is evident that kinetic considerations [54-57] cannot be ignored since kinetic instabilities observed in Si homoepitaxy [58] give rise to similar morphological evolutions.

At higher misfit ($\epsilon \sim 1.2\%$, $x \sim 0.3$), square isotropic mounds (with lateral size $L \sim 100$ nm) nucleate, superimposed on the rough surface. These islands, usually called "huts", adopt pyramidal shape with the four bases oriented along $\langle 100 \rangle$ directions and the four facets approximately corresponding to (105) facets [23]. GIXRD analysis proves the absence of elastic relaxation in such "hut" islands [19]. In this regime, the island evolution with the thickness differs from the evolution with the misfit (Fig. 4). Indeed, at increasing deposited thickness, there occurs a shape transition from square based islands (Fig. 4(a)) to elongated rectangular based

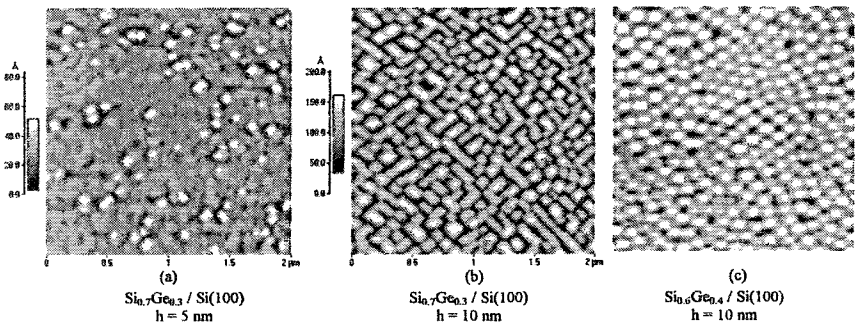


Figure 4. AFM image of $\text{Si}_{1-x}\text{Ge}_x$ surface for (a) $x = 0.3$; $h = 5$ nm (b) $x = 0.3$; $h = 10$ nm and (c) $x = 0.4$; $h = 10$ nm. Scan size is ~ 2 μm .

islands (Fig. 4(b)), while an increasing misfit induces an increasing density of square based islands (Fig. 4(c)).

In order to determine the stability of such "hut" island shape, we have followed their morphological evolution during annealing at 550 °C. Starting from a ripplelike as-grown surface, formation of fully strained "hut" islands occurs after 1h30 annealing (no elastic relaxation was detected at this stage). After 18 h annealing, islands evolve towards large isolated "huts" that exhibit well-defined (105) facets (Fig. 5(a)). Elastic relaxation measured in these large hut islands ($\Delta\epsilon_{xx} \sim 0.25\%$) is very low (Fig. 5(b)). They are consequently still highly strained (about 0.75 %).

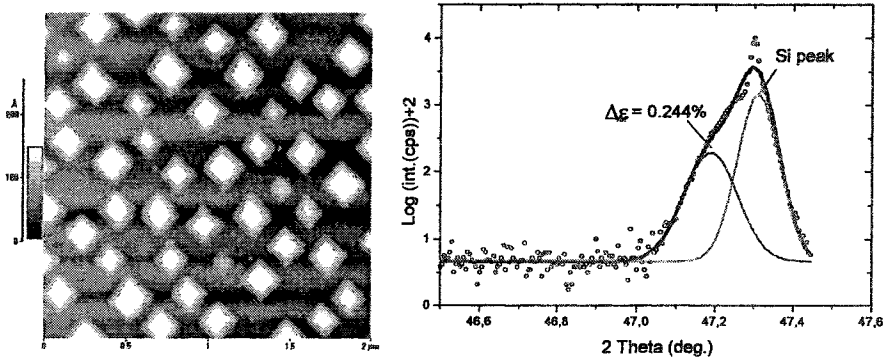


Figure 5. AFM image (a) and GIXRD spectrum (b) of "hut" islands obtained after 18 hrs annealing at 550 °C of a $\text{Si}_{0.75}\text{Ge}_{0.25}$ ($h = 10$ nm).

No further evolution neither of the morphology nor of the elastic relaxation occurs during subsequent 46 h annealing. This proves that large "huts" represent an equilibrium steady state and we suggest that their morphology is stabilized by the compressive biaxial stress applied by the substrate to the islands. If this is the case, (105) facets would belong to the equilibrium shape of $\text{Si}_{1-x}\text{Ge}_x$ under compressive stress. Thermal stability of hut islands (during long term annealing) was also reported in [62]. However this is in contradiction with conclusions of [13,63] which believe that huts only provide a kinetic favorable path from 2D to stable macroscopic islands. In our scheme of growth, these results, that seem contradictory, are in fact compatible as will be shown below (see *regime III* description). Nevertheless, further experiments are needed to determine the exact origin of hut island formation.

In *regime III*, coexistence of "huts" and "domes" is observed (Fig. 6) [64,65]. The two island groups are characterized by different aspect ratios (~ 0.15 and ~ 0.04 for "domes" and "huts" respectively) and different shapes: "domes" have mainly round shape with their larger facets approximately corresponding to $\{113\}$ planes. Several other side orientations were found at the dome surface, but they could not be accurately determined by AFM. For a detailed description of the dome shape see [64]. The respective density of "huts" and "domes" varies with the experimental

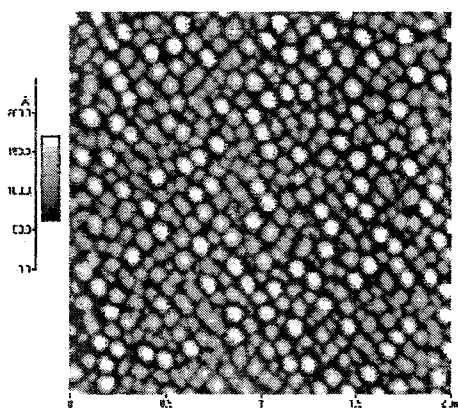


Figure 6. AFM image of the coexistence of "huts" and "domes" for $\text{Si}_{0.6}\text{Ge}_{0.4}$ ($h = 5$ nm).

process, is accompanied by a dramatic increase of the relaxation level ($\Delta\epsilon_{xx} \sim 0.85\%$) (Fig. 7). This suggests that the "hut"- "dome" transition is mainly driven by stress relaxation and that hut islands (and in particular (105) facets) are destabilized by the elastic stress relaxation. As a consequence as the stress relaxation process takes place, the (105) decrease in size at the expense of (113) and (111) facets that are the stable facets, present in the equilibrium shape of bulk Si (without stress).

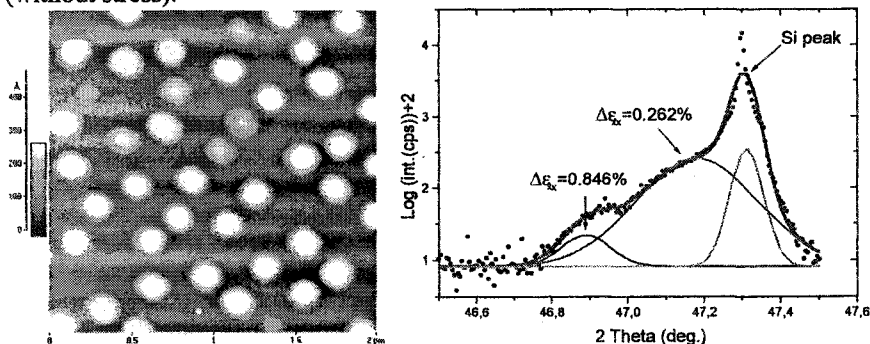


Figure 7. AFM image (a) and GIXRD spectrum (b) of "hut" and "domes" stabilised during the hrs annealing at 550°C of a $\text{Si}_{0.6}\text{Ge}_{0.4}$ ($h = 5$ nm).

In this scheme of growth every step accompanied by stress relaxation will induce the "hut"- "dome" transition. This could explain the discrepancy (reported above) between bibliographic results, on the role of annealing on the hut/dome transition. Indeed, at a lower level of stress, strained islands huts could be a steady state morphology (with a low level of stress relaxation) while at a higher level of

conditions: "domes" are favoured in the higher stress regime, while "huts" are favoured in the lower stress regime. The most striking result here is that a much higher level of elastic relaxation was measured in "domes". For instance, $\Delta\epsilon_{xx} \sim 0.78\%$ was found in an as-grown $\text{Si}_{0.5}\text{Ge}_{0.5}$ layer with $h = 5$ nm ($\epsilon = 2.1\%$). In this growth regime, as-grown square islands also transform during annealing (long term annealing at 550°C) into larger round shaped domes that constitute the steady state morphology of this growth regime. This transition, based on a ripening

stress, steady state morphology would consist of relaxed dome islands (because stress relaxation process is energetically favored). So, even if metastable huts could form during growth in this higher stress regime, they will rapidly transform into domes, with a small input of energy gained during annealing. Also during higher temperature annealing the gain of thermal energy will allow dislocation to nucleate and will lead to the hut (strained)/dome (relaxed) transition.

In *regime IV*, a bimodal size distribution of domes is observed. They correspond to dislocated and coherent structures respectively. The latter ones are similar to those described in the previous section. Hut islands are never observed in this regime. The steady state morphology consists of larger relaxed islands. Such islands are not relevant for this paper. For a comprehensive review on the dislocation nucleation see [41,66].

4 Acknowledgements

We thank the EC project SiGeNet (№ IHP-RTN-99-1) for financial support.

References

1. The International Technology Roadmap for Semiconductors, 1999 Edition (Semiconductor Industry Association, San Jose, CA, 1999).
2. Likharev K. K., *Nanotechnology* **10** (1999) 159.
3. Sze S. M., In *Future Trends in microelectronics. The road ahead*, ed. by S. Luryi, Xu J., Zaslavsky A. (John Wiley and sons, 1999) 291.
4. Watanabe H., In *Future Trends in microelectronics. The road ahead*, ed. by S. Luryi, Xu J., Zaslavsky A. (John Wiley and sons, 1999) 33.
5. Likharev K. K., *Proc. IEEE* **87** (1999) 606.
6. Yano K., Ishii T., Hashimoto T., Kobayashi T., Murai F., Seki K., *Proc. IEEE Int. Electron Devices Meeting* (1993) 541; Yano K., Ishii T., Hashimoto T., Kobayashi T., Murai F., Seki K., *IEEE Trans. Electron. Devices* **41** (1994) 1628.
7. Tiwari S., Rana F., Hanafi H., Hartstein A., Crabbé A. F., Chan K., *Appl. Phys. Lett.* **68** (1996) 1377.
8. Hanafi H. I., Tiwari S., *IEEE Trans. Electron. Devices* **43** (1996) 1553.
9. Banerjee S., Nozaki S., Morisaki H., *Appl. Phys. Lett.* **76** (2000) 445.
10. Pchelyakov O. P., Bolkhovityanov Y. B., Dvurechenskii A. V., Nikiforov A. I., Yakimov A. I., Voigländer B., *Thin Solid Films* **367** (2000) 75.
11. Mo Y.-W., Savage D. E., Swartzentruber B. S., Lagally M. G., *Phys. Rev. Lett.* **65** (1990) 1020.
12. Hammar M., LeGoues F. K., Tersoff J., Reuter M. C., Tromp R. M., *Surf. Sci.* **349** (1996) 129.

13. Kamins T. I., Carr E. C., Williams R. S., Rosner S. J., *J. Appl. Phys.* **81** (1997) 211.
14. Liu F., Wu F., Lagally M. G., *Chem. Rev.* **97** (1997) 1045.
15. Sutter P., Lagally M. G., *Phys. Rev. Lett.* **84** (2000) 4637.
16. LeGoues F. K., Reuter M. C., Tersoff J., Hammar M., Tromp R. M., *Phys. Rev. Lett.* **73** (1994) 300.
17. Berbezier I., Gallas B., Ronda A., Derrien J., *Surf. Sci.* **412/413** (1998) 415.
18. Volpi F., Portavoce A., Ronda A., Shi Y., Gay J. M., Berbezier I., *Thin Solid Films* **380** (2000) 46.
19. Ronda A., Abdallah M., Gay J. M., Stettner J., Berbezier I., *Appl. Surf. Sci.* **162/163** (2000) 576.
20. Gao H., Mech J., *Phys. Solids* (1994) 741.
21. Jesson D. E., Chen K. M., Pennycook S. J., *MRS Bulletin XXI* (1996) 31.
22. Springholz G., Bauer G., *Phys. Rev. B* **48** (1993) 10998.
23. Mo Y. M., Savage D. E., Swartzentruber B. S., Lagally M. G., *Phys. Rev. Lett.* **65** (1990) 1020.
24. Cullis A. G., *MRS Bulletin XXI* (1996) 21.
25. Grilhé J., *Acta Metall. Mat.* **41** (1993) 909.
26. Tersoff J., Le Goues F. K., *Phys. Rev. Lett.* **72** (1994) 3570.
27. Müller P., Kern R., *Appl. Surf. Sci.* **102** (1996) 6.
28. Ratsch C., Zangwill A., Smilauer P., Vvedensky D. D., *Phys. Rev. Lett.* **72** (1994) 3194.
29. Srolovitz D. J., *Acta Metall.* **37** (1989) 621.
30. Pidduck A., Robbins D., Cullis A., Leong W., Pitt A., *Thin Solid Films* **222** (1992) 78.
31. Eaglesham D. J., Gossmann H. J., Cerullo M., *Mat. Res. Soc. Symp. Proc.* **198** (1990) 51.
32. Hull R., Bean J. C., Peticolas L. J., Bahnck D., Weir B. E., Feldman L. C., *Appl. Phys. Lett.* **61** (1992) 2802.
33. Pchelyakov O. P., Markov V. A., Nikiforov A. I., Sokolov L. V., *Thin Solid Films* **306** (1997) 299.
34. Asaro R. J., Tiller W. A., *Metall. Trans.* **3** (1972) 1789.
35. Grinfeld M. A., *J. of Intelligent Mat. Syst. and Struct.* **4** (1993).
36. Bermond J. M., Métois J. J., Egéa X., Floret F., *Surf. Sci.* **330** (1995) 48.
37. J. W. Matthews, *J. Vac., Sci. Technol.* **12** (1975) 126.
38. Hull R., Bean J. C., *Critical Reviews in Solid State and Mat. Sci.* **17** (1992) 507.
39. Kamat S. V., Hirth J. P., *J. Appl. Phys.* **67** (1990) 6844.
40. Le Goues F. K., Copel M., Tromp R. M., *Phys. Rev. Lett.* **63** (1989) 1826.
41. Le Goues F. K., *MRS Bulletin XXI* (1996) 38.
42. Eaglesham D. J., Kvam E. P., Maher D. M., Humphreys C. J., Bean J. C., *Phil. Mag. A* **59** (1992) 2802.

43. Albrecht M., Christiansen S., Strunk H. P., Hansson P. O., Bauser E., *Solid State Phenomena* **32/33** (1993) 433.
44. Mathews J. W., Jackson D. C., Chambers A., *Thin Solid Films* **26** (1975) 129.
45. Van der Merve J.H., *J. Appl. Phys.* **34** (1963) 117.
46. Mathews J. W., Blakeslee A. E., *J. Of Cryst. Growth* **27** (1974) 118.
47. Berbezier I., Gallas B., Derrien J., *Surf. Rev. Lett.* **5** (1998) 133.
48. Deelman P. W., Thundat T., Schowalter L. J., *Appl. Surf. Sci.* **104/105** (1996) 510.
49. Gallas B., Berbezier I., Ronda A., Derrien J., *Thin Solid Films* **294** (1997) 22.
50. Wu F., Chen X., Zhang Z. Y., Lagally M. G., *Phys. Rev. Lett.* **74** (1995) 574.
51. Alerhand O. L., Vanderbilt D., Meade R. D., Joannopoulos J. D., *Phys. Rev. Lett.* **61** (1988) 1973.
52. Zong L., Hojo A., Matsushita Y., Aiba Y., Hayashi K., Takeda R., Shirai H., Saito H., Matsushita J., Yoshikawa J., *Phys. Rev. B* **54** (1996) R2304.
53. Mukherjee S., Pehlke E., Tersoff J., *Phys. Rev. B* **49** (1994) 1919.
54. Smilauer P., Vvedensky D. D., *Phys. Rev. B* **52** (1995) 14263.
55. Ratsh C., Smilauer P., Vvedensky D. D., Zangwill A., *J. Phys. I France* **6** (1996) 575.
56. Siegert M., Plischke M., *Phys. Rev. E* **50** (1994) 917.
57. Snyder C. W., Mansfield J. F., Orr B. G., *Phys. Rev. B* **46** (1992) 9551.
58. Pierre-Louis P., Misbah C., *Phys. Rev. Lett.* **76** (1996) 4761.
59. Rost M., Smilauer P., Krugg J., *Surf. Sci.* (1996).
60. Lee N. E., Cahill D. G., Greene J. E., *Phys. Rev. B* **53** (1996) 7876.
61. Schelling C., Springholz G., Schäffler F., *Phys. Rev. Lett.* **83** (1999) 995.
62. Floro J. A., Chason E., Freund L. B., Twisten R. D., Hwang R. Q., Lucadamo G. A., *Phys. Rev. B* **59** (1999) 1990.
63. Ross F. M., Tromp R. M., Reuter M. C., *Science* **286** (1999) 1931.
64. Medeiros-Ribeiro G., Bratkovski A. M., Kamins T. I., Ohlberg D. A. A., Williams R. S., *Science* **279** (1998) 353.
65. Goryll M., Vescan L., Schmidt K., Mesters S., Lüth H., Szot K., *Appl. Phys. Lett.* **71** (1997) 410.
66. Eaglesham D. J., Kvam E. P., Maher D. M., Humphreys C. J., Bean J. C., *Phil. Mag. A* **59** (1989) 1059.

INVITED

STRESS AND STRAIN DISTRIBUTIONS IN Ge DOTS ON Si(001) BY MOLECULAR DYNAMICS SIMULATION.

P. RAITERI, F. VALENTINOTTI, L. MIGLIO

*INFN and Università di Milano-Bicocca
V. Cozzi 53, I-20125 Milano, Italy*

E-mail: Leo.Miglio@mater.unimib.it

By applying molecular dynamics simulation with a three-body potential for SiGe we have studied the elastic interaction between realistic SiGe dots and Si(001) substrate. Stress and strain distributions were computed indicating a complex and deep deformation of the substrate and a slight relaxation in the Ge pyramid.

1 Introduction

In recent years much interest has been focused on low dimensional semiconductor structures. In particular, it is shown that Si-Ge heterostructures promise wide applications in new micro- and opto-electronic devices [1]. Since the first observation of Ge dots on Si(001) grown by molecular beam epitaxy at 475 °C [2,3], a lot of investigations [4-6] have been performed in order to study the growth mechanism and physical properties of these nanostructures. Actually, Ge epitaxially grows on Si(001) following a Stranski-Krastanov (SK) mechanism [7], and the evolution of the island morphology with coverage is quite well documented.

By disregarding the effects of Si-Ge intermixing, which take place at temperatures higher than 650 °C, the morphology of Ge islands on top a wetting layer as thick as 3-4 monolayers (MLs) can be divided in to two categories: pyramids with {105} facets and domes with a more complex faceting. The lateral dimensions for the Ge islands typically range from 10 nm to 25 nm or from 35 nm to 60 nm for the pyramids, and from 60 to 80 nm for the domes. The {105} pyramids always appear first, but thermal annealing or further deposition of Ge allows transformation of these islands into domes. Still, the reasons for the bimodal distributions of the pyramids and their appearance in the early stages of growth are matter of controversy. Only very recently Vailionis *et al.* [8] could take STM pictures of <110> flat islands with a small aspect ratio (0.04) that seem to act as precursors for the pyramid nucleation. The elastic energy can be very important in interpreting the relative stability of the Ge dots with respect to flat (2D) islands, and in establishing whether the SK growth mechanism is due to thermodynamics or kinetic reasons.

While many experimental data are available, few theoretical work, primarily based on the theory of elastic continuum, has been produced. In this paper we study the stress and strain distributions in the Ge/Si(001) systems by performing molecular dynamics (MD) simulations with a suitable interatomic potential. Our results are presented at the atomic resolution, a scale that cannot be achieved by experimental measurements.

2 Method

We have performed MD simulations on realistic Ge dots on Si(001) by an original improvement of the ANSI-C xmd code of the Connecticut University [9]. The Si-Ge parameterization [10] was implemented in the Tersoff potential [11], where the energy is expressed as a sum of the atomic pair interactions

$$E = \frac{1}{2} \sum_{i \neq j} f_C(r_{ij}) [f_R(r_{ij}) + b_{ij} f_A(r_{ij})], \quad (1)$$

where b_{ij} includes many body interactions. This coefficient is the sum over the angular contributions of each atom that is bound either to i or to j . The Tersoff potential for Si and Ge can reproduce well the elastic constants for elemental diamond-like structures, with a maximum error of 10 %, but for the slight discrepancy in the estimation of the transverse acoustic mode dispersion [12]. It is clear that the Tersoff potential cannot reproduce the chemical reactivity of Si and Ge, still a suitable definition of the parameters for the heterogeneous interactions [10] allows for a good description of the ground state properties of SiGe systems.

In order to take into account millions of atoms, we implemented the linked-cell algorithm in the calculation of the nearest neighbours lists [13]. This feature upgrades the scalar code to simulate, in a reasonable time, systems as large as 1.5 million atoms for time scales of the order of few hundreds of picoseconds. In Fig. 1 we report a comparison between the original xmd code (with the usual double loop for the calculation of the Verlet list [13]) and the linked cell version. It is evident that the linked-cell approach gives a linear dependence of the simulation time with respect to the number of atoms.

Finally we developed the computational procedure to evaluate the atomic stress and strain. According to [14] the atomic stress can be computed as:

$$\sigma_{\alpha\beta}(i) = -\frac{1}{\Omega} \left[\frac{p_i^\alpha p_j^\beta}{m_i} + \frac{1}{4} \sum_j (r_{ij}^\alpha f_{ij}^\beta + r_{ij}^\beta f_{ij}^\alpha) \right], \quad (2)$$

where $(\alpha, \beta) \equiv (x, y, z)$, m_i and p_i are the atomic mass and momentum, r_{ij} is the distance from atom i to j , f_{ij} is the force that atom j exerts on atom i and Ω is the average atomic volume. The first term of equation (2) can be neglected because our measurements are always performed either at 0 K or on the time-average positions.

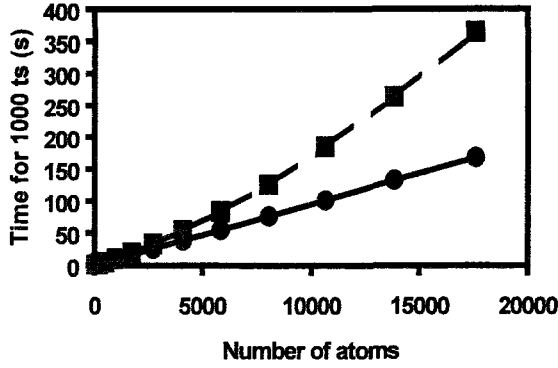


Figure 1. Time elapsed for 1000 ts vs. the number of atoms in the simulation cell. Circles (●) indicate the linked-cell algorithm, squares (■) the usual double loop on the atoms.

According to the elastic continuum theory and taking into consideration the cubic symmetry of the diamond-like structure of both elements, a very simple model to compute the atomic strain matrix elements was developed by considering the tetrahedron formed by the nearest neighbours of each atom as the fundamental unit. Here we define the atomic strain as the deformation of such a tetrahedron, which can be directly derived from the displacement of the nearest neighbour shell with respect to the atom placed in the center of the tetrahedron. Thus, the matrix element of the strain tensor is:

$$\varepsilon_{\alpha\beta}(i) = \frac{1}{4} \sum_j \frac{\Delta r_{ij} \cdot \hat{\alpha}}{r_{ij}^0 \cdot \beta}, \quad (3)$$

where Δr_{ij} is the variation of the distance between atom i and atom j with respect to the perfect lattice (r_{ij}^0), both projected on the α and β directions.

We used a time step of 2 ps and the sample was annealed first for 30 ps at 300 K, then for 30 ps at 1200 K. High temperature annealing is indicated in order to safely reach an equilibrium redistribution of the elastic stress. Afterwards, we cooled down the system to 300 K and a 10 ps NVT thermalization has been performed followed by a 10 ps NVE run in order to compute the equilibrium positions. We applied the periodic boundary conditions only in the x and y direction. The two bottom Si atomic planes were fixed to their equilibrium position at 300 K to have only one free surface: the one formed by the wetting layer (WL) and the {105} pyramid on top.

3 Results

The Ge dot, with lateral dimensions comparable with the experiments (27 nm) [4], and a wetting layer (4 monolayers) are placed above a square Si substrate with 2D periodic boundary conditions. The substrate side and thickness are taken to be

54 nm and 8.1 nm, respectively. For sake of comparison we also investigated the stress and strain distributions in a sample with the same amount of Ge atoms in the layer by layer growth mode [7], known as Frank-van der Merwe mechanism. For the free surfaces we observed a spontaneous (2x1) reconstruction. Actually, we also studied the stability of the (2x8) reconstruction of the (001) surface and we found that, for a wetting layer as thick as 3 MLs, this configuration is more stable of the (2x1) reconstruction by $0.021 \text{ eV}/a^2$ (where a is the surface lattice parameter of the unreconstructed Si(001)). Still we did not include the (2x8) reconstruction in this preliminary calculation of the elastic properties, since our annealing at high temperatures destroys the reconstruction pattern.

In the following we show the particular features of the strain and stress maps and the deep penetration of the deformation field throughout the substrate. We also demonstrate the importance of a thick Si substrate for realistic simulations of Ge/Si(001) stability.

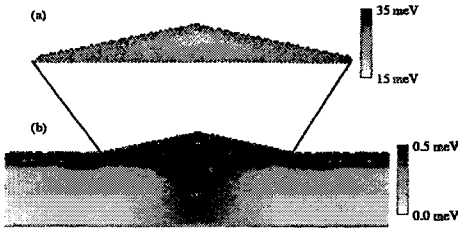


Figure 2. Elastic energy map computed in the (010) cross-section with the zero energy equal to the bulk Ge energy (a) and to the bulk Si energy (b).

A new graphical tool has been developed to visualize the results of our simulations. We added the possibility of drawing 2D maps of selected cross-sections with a suitable choice of black and white (or color) scales for stress, strain and potential energy distributions (see for example Figs. 2,3). In this paper we report only black and white figures. Each atom displays a gray scale that linearly depends on its strain (or stress) value. Unfortunately, stress and strain can assume both positive and negative values so the zero is set to a particular gray value. To help the interpretation we added an arrow, which points out the zero, next to the scales and plus and minus signs on Fig. 4.

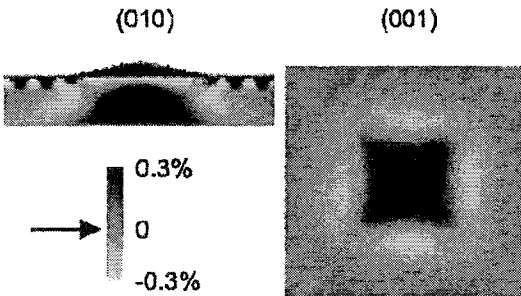


Figure 3. E_{zz} strain component computed in two different cross-sections.

in the Ge dots. Indeed the pyramids do not have any lateral constraints and this allows for a sensible relief of the compressive stress due to the lattice mismatch between the Si substrate and the epitaxially grown Ge. This relaxation is hardly

The first issue we want to address is the strain relaxation

visible in the stress and strain maps whereas it is clearly evident in the elastic energy maps, shown in Fig. 2(a), where we displayed the elastic energy stored in the dot and in the substrate. We also used two different scales to show the features both in the pyramid and in the substrate. In fact, in Fig. 2(b) it is clearly seen the deformation induced by the Ge dot in the substrate.

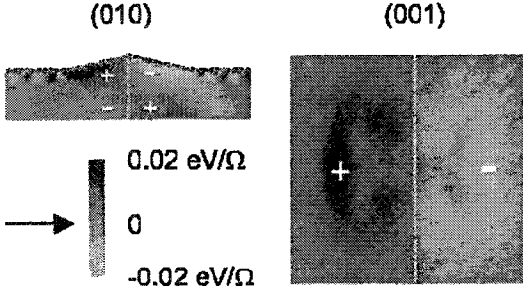


Figure 4. σ_{xz} stress shear component computed in two different cross-sections.

present an expanded region, exactly below the dot (big and almost black region), surrounded by a compressed square corral, which is likely to provide a quantum confinement just in the silicon substrate. In Fig. 4 it is fairly evident a twofold symmetry in the (010) and (001) stress maps. All these features can be directly related to the substrate bending since the opposite sign of σ_{xz} indicates that the two parts undergo shear deformations in opposite directions.

The substrate bending cannot be attributed to a model artifact and corresponds to some experimental evidences. In fact, this issue is in a perfect agreement with

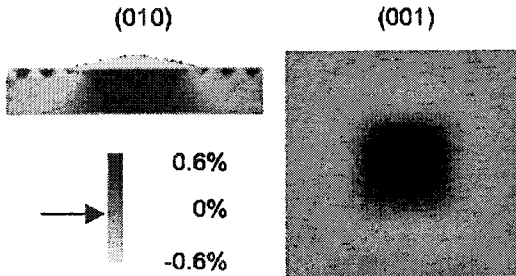


Figure 5. Hydrostatic strain computed in two different cross-sections.

conclude that a real expansion of the Si lattice is produced just below the Ge dot.

This feature is absent in the sample with the layer by layer growth, since strain and stress are estimated to be almost zero in the lower part of the substrate.

One next feature is the complexity of the deformation field induced in the substrate by the {105} pyramid. In Figs. 3, 4 we show the ε_{zz} and σ_{xz} components of the strain and stress tensors, respectively, computed in a (010) cross-section passing through the pyramid apex (left) and in a (001) cross-section passing in the middle of the wetting layer (right). In Fig. 3 we

present an expanded region, exactly below the dot (big and almost black region), surrounded by a compressed square corral, which is likely to provide a quantum confinement just in the silicon substrate. In Fig. 4 it is fairly evident a twofold symmetry in the (010) and (001) stress maps. All these features can be directly related to the substrate bending since the opposite sign of σ_{xz} indicates that the two parts undergo shear deformations in opposite directions.

The substrate bending cannot be attributed to a model artifact and corresponds to some experimental evidences. In fact, this issue is in a perfect agreement with x-ray diffraction [15] and TEM [3] measurements and with previous theoretical predictions [14]. Furthermore, that feature is used by Floro *et al.* [16] to follow the dots nucleation and shape transformation by monitoring the substrate bending with a suitable grid of laser beams. By considering the hydrostatic deformation, Fig 5, we

In Fig. 6 we show ϵ_{xx} and ϵ_{zz} computed along a rod passing through the pyramid apex. Here we can see a quantitative estimation of the features

previously described, *i.e.* the in-plane expansion of the Si substrate near the interface (8 nm), the expansion toward z in the lower part of the sample and the strain relief in the pyramid. In particular, one can notice that the ϵ_{zz} component is still different from zero at the bottom of the Si substrate. Our data reported in Fig. 6 are in a perfect agreement with the ones reported in [14].

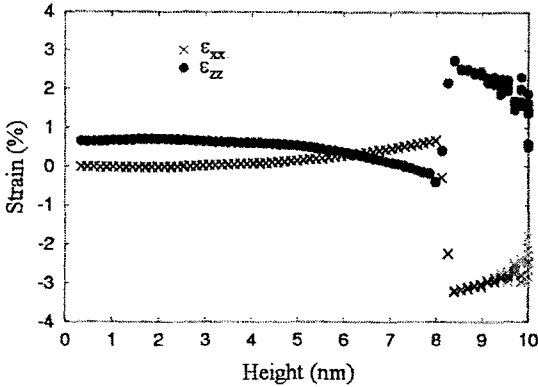


Figure 6. XX and ZZ strain components (upper panel) and the trace of the stress matrix (lower panel) computed in a tube passing through the dot apex.

4 Conclusions

We conclude that our preliminary investigation of the elastic properties of Ge/Si(001) dot by pointing out that a complex, far-reaching substrate deformation is present, probably affecting the dot thermodynamics to a larger extent than that was previously considered. Moreover, quantum confinement in the Si substrate seems to be very likely and deserves suitable quantitative estimations.

5 Acknowledgements

We gratefully acknowledge the graphical support of Dr. Dmitri Migas (INFM unit of Milano-Bicocca) and helpful discussions with Dr. Massimo Celino (HPCN Project-ENEA Rome).

References

1. *Properties of Silicon Germanium and SiGe:Carbon*, ed. by Kasper E., Lyutovich K.(INSPEC, London, 2000).
2. Mo Y.-M., Savage D. E., Swartzentruber B. S., Lagally M. G., *Phys. Rev Lett.* **65** (1990) 1020.

3. Eaglesham D. J., Cerullo M., *Phys. Rev Lett.* **64** (1990) 1943.
4. Chaparro S. A., Zhang Y., Druker J., Chandrasekhar D., Smith D. J., *J. Appl. Phys.* **87** (2000) 2245.
5. Kamins T. I., Medeiros-Ribeiro G., Ohlberg D. A. A., Stanley Williams R., *J. Appl. Phys.* **85** (1999) 1159.
6. Chen Y., Washburn J., *Phys. Rev Lett.* **77** (1996) 4046.
7. Luth H., *Surfaces and Interfaces of Solid Material* (Springer-Verlag, Berlin, Heidelberg, New York, 1995).
8. Vailionis A., Cho B., Glass G., Desjardins P., Cahill D. G., Greene J. E., *Phys. Rev. Lett.* **85** (2000) 3672.
9. Tersoff J., *Phys. Rev. B* **39** (1989) 5566.
10. Rifkin J. <http://www.ims.uconn.edu/centers/simul>.
11. Tersoff J., *Phys. Rev. Lett.* **56** (1986) 632.
12. Moriguchi K., Shintani A., *Jpn. J. Appl. Phys.* **37** (1998) 414.
13. Allen M. P., Tildesley D. J., *Computer Simulation of Liquids* (Oxford University Press, New York, 1989).
14. Yu W., Madhukar A., *Phys. Rev Lett.* **79** (1997) 905.
15. Williams A. A., Thornton J. M., MacDonald J. E., van Silfhout R. G., van der Veen F., Finney M. S., Johnson A. D., Norris C., *Phys. Rev. B* **43** (1991) 5001.
16. Floro J. A., Chason E., Freund L. B., Twisten R. D., Hwang R. Q., Lucadamo G. A., *Phys. Rev. B* **59** (1999) 1990.

LIGHT EMISSION FROM SEMICONDUCTING SILICIDE NANOSTRUCTURES IN SILICON

K. J. KIRKBY, M. LOURENÇO, T. M. BUTLER, K. HOMEWOOD, C. N. MCKINTY

*School of Electronics, Computing and Mathematics, University of Surrey
Guildford, Surrey, GU2, 5XH, England*

E-mail: k.kirkby@surrey.ac.uk

It has recently been shown that room temperature electroluminescence can be obtained from silicon containing nanostructures of β -FeSi₂. These structures have been prepared using either Ion Beam Synthesis (IBS) or Reaction Deposition Epitaxy (RDE). For the IBS structures a maximum in the EL intensity is found for doses $\sim 1.5 \times 10^{16}$ Fe/cm². The quenching of the EL is found to vary with both the doping of the p-type layer and hence the proximity of the precipitates to the depletion region of the p-n junction and the thickness of the silicon overlying the precipitates where radiative recombination can occur. The optimum results, in terms of EL quenching are found for the highest p-type doping (1×10^{18} cm⁻³) and for the thickest p-type layer (1 μ m). For the RDE sample where the β -FeSi₂ nanostructures are fabricated at the junction between the p- and n- type regions, the EL increased superlinearly with increasing injected current density, with a reasonable EL signal above 10 A/cm². These results indicate that by reducing the defect density in the silicon surrounding the β -FeSi₂ nanostructures and optimising the device structure, it should be possible to form practical silicon based light emitting devices incorporating β -FeSi₂ in the next few years

1 Introduction

The development of silicon based integrated circuit technology has more or less followed Moore's law for the past three decades. Moore's law states that *the number of transistors that can be placed on the same area of a microprocessor doubles every eighteen months*. The point is now being reached, however, where the delay time in the devices and interconnects, means that further miniaturization and increases in packing density are posing severe technological problems and are not yielding the increases in circuit speed required for the next generation of integrated circuits. One solution to these problems would be to use silicon based optoelectronics, however, the indirect band gap of silicon would at first sight appear to preclude this as a possibility. The worldwide investment in silicon technology, however, has meant that significant research effort has been directed at making silicon-based optoelectronics a reality. Several solutions have been proposed. These include:

- SiGe superlattice structures [1]
- Er implanted silicon [2]

- Porous silicon [3]
- Semiconducting silicides (e.g. β -FeSi₂, Ru₂Si₃) [4-10]

Table 1 explores the emission characteristics of these various alternatives, lists how they are fabricated and compares their reliability and compatibility with silicon integrated circuit manufacture. It is apparent that not all the structures emit light at the same wavelength. The wavelength of 1.5 μ m is seen as particularly advantageous since this is the wavelength window currently employed by optical fibres. In this paper we will concentrate on the semiconducting silicides, in particular, β -FeSi₂, which emits light at 1.5 μ m.

Table 1. Comparison of the different routes for light emission from silicon.

Material	Wavelength (λ) linewidth (LW)	Quantum efficiency	Time constant	Reliability	Technology	IC compatible
Si-Ge	λ 1.3 μ m LW 0.1 μ m @ RT 0.03 μ m @ 100 K	1×10^{-3} (RT) 1×10^{-4} (150K)	50-100 ns	high	MBE CVD	yes
Porous Si	λ Visible (650-800 nm) LW Broad	2×10^{-3} (RT)		very low	Etching	no
Er in Si	λ 1.54 μ m LW sharp	1.5×10^{-4} (RT) 1×10^{-2} expected	$\geq 1 \mu$ s	high	Ion implant MBE	yes
β -FeSi ₂	λ 1.55 μ m LW 0.03 eV	1×10^{-3} (80K) RT meas	< 40 ns	high	IBS RDE MBE, MBA	yes
Ru ₂ Si ₃	λ 1.55 μ m LW sharp* * anticipated	?	?	?	IBS MBE, MBA	yes

Miglio [11] has likened the recent history of research on β -FeSi₂ to that of the stockmarket rollercoaster with periods of euphoria followed by dark despair followed again by a euphoric rise. In the mid 1990's debate was focussed on the nature of the band gap in β -FeSi₂. *Ab initio* band structure calculations [12-13] predicted an indirect band gap, with a direct transition very close to it in energy. This was confirmed by some experimental observations [14]. Other experimental results, including our own studies suggested that the band gap was direct [15-20]. Debate raged in the literature with the photoluminescence attributed by the "*direct band gap group*" as coming from the β -FeSi₂, being dismissed by the "*indirect group*" as being simply a manifestation of the silicon D lines [21]. Both sides appeared entrenched - in 1997, however the first results were published [22] on an electroluminescent device operating at 1.5 μ m, in which a layer of β -FeSi₂ precipitates had been fabricated above a silicon p-n junction. More recent theoretical studies, by Miglio and Meregalli [11,23] have concluded that the extreme sensitivity of the electronic bands to lattice deformation and the strong electron phonon coupling may account for the different experimental observations.

They concluded that the growth conditions may be critical in determining whether the β -FeSi₂, so formed, has a direct or indirect band gap.

The fundamental requirements for optoelectronic devices in silicon, are an emitter, a method of guiding the light within the silicon and a detector. This paper will concentrate on the emitter by examining electroluminescence data from β -FeSi₂ nanostructures, in silicon, fabricated by different techniques.

2 Electroluminescence from structures containing β -FeSi₂ precipitates

2.1 Introduction

To date, two methods [22,24,25] have been successfully employed to achieve room temperature electroluminescence (albeit rather weak) from silicon based structures incorporating precipitates of β -FeSi₂. These are:

- Ion beam synthesis (IBS) [22,24] – which uses high dose Fe⁺ implantation, at elevated temperatures, (500-600 °C) into a silicon p-n junction, followed by a 900 °C, 18 h anneal in a nitrogen ambient.
- Reaction deposition epitaxy (RDE) [25] – using this technique, Suemasu et al. [25] deposit a thin (~ 10 nm) continuous layer of epitaxial β -FeSi₂ on a pre-grown p-n junction. After which, the sample is annealed in ultra high vacuum at 850 °C for 1 h and then 0.3 μ m of p-type silicon is deposited, at 500 °C by molecular beam epitaxy (MBE). The structure is then annealed in an argon ambient at 900 °C for 14 h.

Table 2 describes the substrates, which were used to fabricate a series of electroluminescent devices using both IBS and RDE. Table 3 details the fabrication

Table 2. Substrate details for electroluminescent devices fabricated by IBS and RDE.

No.	Method	Substrate	First layer n ⁺ -type Thickness, μ m Arsenic concentration, cm ⁻³	Second layer p ⁺ -type Thickness, μ m Boron concentration, cm ⁻³
1	IBS	n-type Sb (100) Si 0.01-0.02 Ohm cm	0.4, 5x10 ¹⁷	0.48, 1x10 ¹⁶
2	IBS	n-type Sb (100) Si 0.01-0.02 Ohm cm	0.4, 5x10 ¹⁸	0.36, 1x10 ¹⁷
3	IBS	n-type Sb (100) Si 0.01-0.02 Ohm cm	0.4 1x10 ¹⁹	0.36, 1x10 ¹⁸
4	IBS	n-type Sb (100) Si 0.01-0.02 Ohm cm	0.4 5x10 ¹⁸	1.0, 1x10 ¹⁷
5	RDE	n-type FZ (100) Si 2000-6000 Ohm cm	1.0, 1x10 ¹⁸	0.3, 1x10 ¹⁶ then 0.7, 1x10 ¹⁸

conditions for samples prepared by IBS and RDE. Schematics of the respective device structures for IBS and RDE are displayed in Fig. 1.

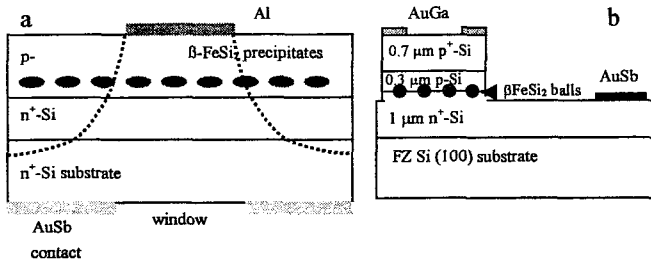


Figure 1. Schematic of the $\beta\text{FeSi}_2/\text{Si}$ light emitting device fabricated by IBS [24] (a) and RDE [25] (b).

The penetration of the depletion region (w) into the p-type region of the device, at zero bias, is calculated for all devices and is shown in Table 3. The distance from

Table 3. Implantation details for samples fabricated by IBS. Calculation of the depletion widths and proximity of the depletion region to the surface and precipitate layer are also shown.

Sample	Dose, Fe/cm^2	Energy, keV	Depletion width (w), μm	Distance surface $\rightarrow$ depletion region (x), μm	Distance ppt $\rightarrow$ depletion region (z), $\text{\AA}$
1	8×10^{15} 1.5×10^{16} 1×10^{17}	180 $R_p \sim 1500 \text{ \AA}$	0.32	0.16	100
2	8×10^{15} 1.5×10^{16} 1×10^{17}	180 $R_p \sim 1500 \text{ \AA}$	0.11	0.25	1000
3	8×10^{15} 1.5×10^{16} 1×10^{17}	180 $R_p \sim 1500 \text{ \AA}$	0.034	0.33	1800
4	1.6×10^{16}	950 $R_p \sim 7100 \text{ \AA}$	0.11	0.89	1800
5	RDE so not applicable		0.33	0	Within depletion region

the surface to the edge of the depletion region (x) is also calculated, where $x = l - w$ and l is the thickness of the epitaxially grown p-type layer. The relative position of the precipitate layer with respect to the depletion region (z) is also shown in Table 3, the precipitate layer is assumed to be centered about the peak of the implanted distribution (at R_p [26]) so $z = x - R_p$. These distances are indicated in the schematic in Fig 2.

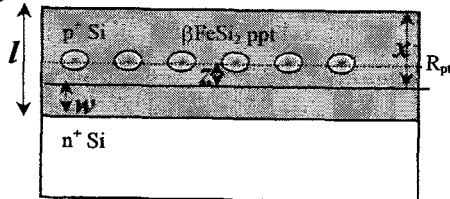


Figure 2. Schematic showing position of depletion region relative to surface and the $\beta\text{-FeSi}_2$ precipitates.

2.2 Ion Beam Synthesis (IBS)

The samples prepared by IBS look at the effects of:

- 1. Dose
- 2. Substrate doping
- 3. Proximity of the precipitate layer to the depletion region and
- 4. The effects of surface layer thickness

For all IBS samples the silicon substrates were maintained at a temperature of between 600 to 675 °C during implantation. Subsequent to implantation annealing was undertaken at 900 °C for 18 h. In all cases, the β -FeSi₂ precipitates were fabricated in the upper p-type layer, which ranged in thickness from 1 μ m for

substrate 4, to 0.48 μ m (substrate 1) to 0.36 μ m for substrates 2 and 3. Substrate 1 had the lowest doping concentration for both layers and hence the widest depletion region [24]. Substrates 2 and 4 differ only in the thickness of the p-type silicon overlayer. For the sample prepared by RDE, the β -FeSi₂ balls are fabricated at the p-n junction and the p-type silicon above them is fully depleted at zero bias.

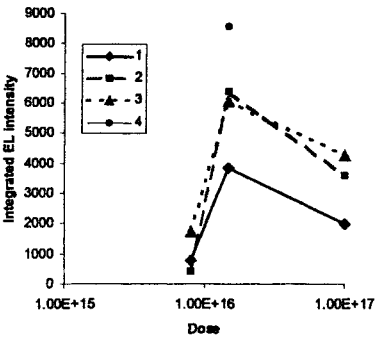


Figure 3. Variation in EL intensity (at 80 K) with dose for substrates 1-4.

Fig. 3 shows how the normalised integrated EL intensity, measured at 80 K, varies with dose and substrate (Tables 2, 3).

From Fig. 3 it is apparent that for all substrates the optimum dose (of those selected) is $1.5 \times 10^{16} \text{ Fe/cm}^2 \pm 10 \%$. Lower doses presumably give a lower EL signal because there are fewer, smaller β -FeSi₂ precipitates. For the higher doses the residual damage, which results from the implantation process and still remains after annealing, is likely to be the cause of the reduced EL intensity. Of the four different substrates, substrate 4 gives the highest EL intensity and substrate 1 the lowest.

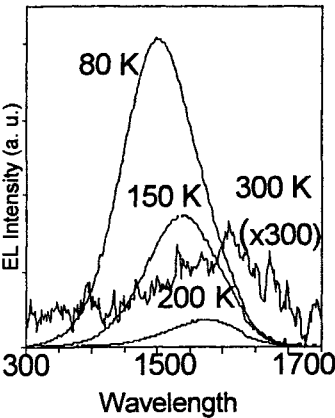


Figure 4. EL from substrate 3 implanted with a dose of $1.5 \times 10^{16} \text{ Fe/cm}^2$.

Fig. 4 shows EL spectra obtained from substrate 3 implanted with a dose of $1.5 \times 10^{16} \text{ Fe/cm}^2$ over the temperature range 80-300 K. As the temperature increases the EL intensity decreases and the width is reduced. To investigate how the EL quenches the normalised integrated intensity of the EL was

measured from 80 K up to room temperature (where possible) for substrates 1 to 4.

Fig. 5 shows the normalised integrated EL intensity versus temperature for substrates 1-4 which have been implanted with a dose of $1.5 \times 10^{16} \text{ Fe cm}^{-2} \pm 10\%$ [24]. For all samples the integrated intensity decreases with increasing temperature.

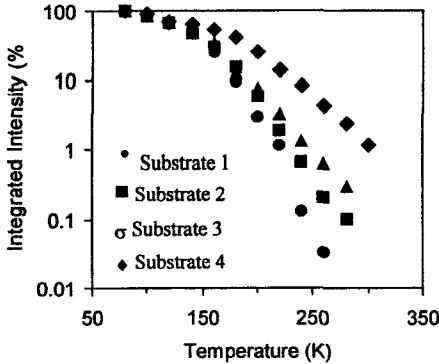


Figure 5. Normalised EL integrated intensity as a function of temperature for substrates 1-4 implanted with $1.5 \times 10^{16} \text{ Fe/cm}^2$.

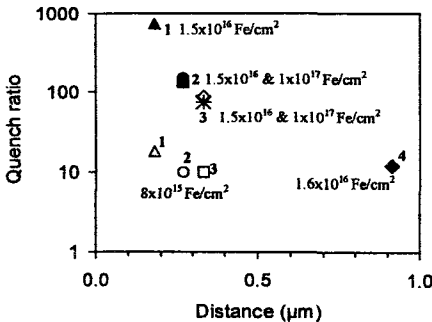


Figure 6. Quench ratio versus distance from the sample surface to the edge of the depletion region. Figures in bold denote substrate number, the other numbers are the implanted dose.

lowest dose ($8 \times 10^{15} \text{ Fe/cm}^2$) have the lowest quench ratio. This group of samples display broad low intensity EL emission at 80 K, which is probably a consequence of the low concentration of $\beta\text{-FeSi}_2$ precipitates present in the samples. All of the substrates do, however, display EL above 280 K and this is probably because less damage was introduced for the lower dose implants than for the higher ones. From Fig. 6 it is again apparent that the quench ratio decreases with increasing doping within the p-type region (substrate 1 $\rightarrow$ 2 $\rightarrow$ 3).

The quench ratio is, defined as the ratio between the integrated EL intensity at 80 K and 240 K (I_{80}/I_{240}).

The slowest quench rate is observed for the substrate with the thickest silicon overlayer (4). For the other substrates (1, 2, 3) the quench ratio decreases with increased doping in the p-type layer. From Table 3 it is apparent that the greater the p-type dopant concentration, the further the $\beta\text{-FeSi}_2$ precipitates are from the edge of the depletion region (thickness z in Table 3 and Fig. 2).

The $\beta\text{-FeSi}_2/\text{Si}$ devices were originally designed so that the synthesised region of $\beta\text{-FeSi}_2$ precipitates lies just outside the depletion region of a $p\text{-n}^+$ junction. Thus, z represents the distance of the precipitates from the depletion region and x the distance from the silicon surface to the top of the depletion region at zero bias. Thus it is that in region x , carrier injection and direct recombination occurs. Fig. 6 plots the quench ratio versus the thickness of region x for all of the samples fabricated using IBS. Examination of Fig. 6 reveals that for the samples implanted at 180 keV, those implanted with the

It is interesting to note from Table 3 that the β -FeSi₂ precipitates in samples 3 and 4 are located at about the same distance from the edge of the depletion region. This would tend to suggest that both the thickness of the silicon overlayer and the proximity of the precipitates to the depletion region are important. It is probable that for the samples implanted at the lower energy (180 keV) the residual damage resulting from the implantation process inhibits the process of carrier injection and direct recombination.

For the samples implanted at higher energies into a thicker p-type layer (substrate 4), there is a larger volume of largely undamaged silicon to facilitate this process. It would be interesting to see how the EL intensity and quench ratio would change if epitaxial p-type silicon were deposited on substrates 1 to 3. It should also be noted in all of this discussion that p-type doping resulting from the presence of the β -FeSi₂ precipitates has not been factored into the calculations of the thickness of the depletion region.

2.3 *Reactive Deposition Epitaxy*

It is rather difficult to directly compare the results obtained from IBS with those recently reported for RDE [25]. This is firstly because the FeSi₂ balls formed by RDE lie across the p-n junction and therefore, by definition within the depletion region at zero bias. There are also no reports of how the EL varies with temperature for the RDE samples and therefore direct comparisons of the quench ratios cannot be made.

The silicon surrounding the FeSi₂ balls, by virtue of its method of deposition contains fewer defects than analogous IBS samples. It was found that the room temperature EL from the RDE sample increased superlinearly with injected current density [25]. The authors suggest that this is because at low bias most of the current flow is through non-radiative centres and it is only when the current flow through these defect levels saturates that radiative recombination can occur. Thus clear room temperature EL is only observed above current densities above 10 A/cm², some 2-3 times higher than for conventional LEDs.

Based on the results from the IBS structures, it is also likely that the RDE EL signal could be enhanced by fabricating the β -FeSi₂ balls just outside the depletion region of the device. It is interesting to note that the EL intensity increases as the depletion region shrinks. The authors suggest that by further reducing the defect density in the RDE samples and by optimising the device structure practical Si based LED's could be obtained in the near future.

3 **Conclusions**

Room temperature EL has been achieved from structures incorporating precipitates of β -FeSi₂, which have been fabricated either by IBS or RDE. For the IBS

structures the optimum dose appears to be in the region of 1.5×10^{16} Fe/cm² for all substrate types. The highest EL intensities are obtained when the β -FeSi₂ precipitates are fabricated within a thick (1 μ m) p-type layer and lie ~ 0.7 μ m below the surface. It is postulated that this is because carrier injection and direct recombination can then occur in relatively undamaged silicon, whereas for the samples implanted at lower energies, this region is much thinner and contains a higher number of defects. The quenching of the EL signal, for the IBS samples, is found to depend on the doping density of the p-type layer and hence the proximity of the β -FeSi₂ precipitates to the depletion region. The best results were achieved for the highest p-type doping density (1×10^{18} B/cm³). Thus, the RT EL from IBS structures may be improved by:

- increasing the thickness of the silicon overlying the β -FeSi₂ precipitates, either by increasing the implantation energy or by growing an epitaxial p-type silicon layer subsequent to implantation;
- increasing the p-type doping in the upper p-type layer. A doping concentration of 1×10^{18} B/cm³ may well be the optimum but this has yet to be established;
- reducing the defect density in the silicon surrounding the β -FeSi₂ precipitates.

For the RDE samples the β -FeSi₂ balls are fabricated across the p-n junction. The RT EL increased superlinearly with injected current density and reasonable EL was observed at room temperature for injection currents above 10 A/cm². By improving the device design and reducing the defect density in both IBS and RDE structures it seems likely that practical silicon based light emitting devices incorporating β -FeSi₂ precipitates will be fabricated in the next few years.

4 Acknowledgements

The authors would like to thank the UK Engineering and Physical Science Research Council (EPSRC) and the EU ESPRIT Advanced Research initiative on Microelectronics (MEL ARI project SILITE 28740) for funding this work.

References

1. Neufeld E., Sticht A., Brunner K., Abstreiter G., Bay H., Buchal C., Holzbrecher H., *Thin Solid Films* **321** (1998).
2. Franzo G., Priolo F., Coffa S., Polman A., Carnera A., *Appl. Phys. Lett.* **64** (1994).
3. Cullis A., Canham L., Williams G., Smith P., Dosser O., *J. Appl. Phys.* **75** (1994) 493.

4. Lange H., Properties and perspectives of semiconducting transition metal silicides, *Mat. Res. Soc. Symp. Proc.* **402** (1996) 307.
5. Lange H., *Phys. Status Solidi (b)* **201** (1997) 3.
6. Borisenko V. *Semiconducting Silicides* (Springer-Verlag, Berlin, 2000).
7. Reeson K. J., Sharpe J., Harry M., Leong D., Kewell A., Chen Y. L., Mckinty C. N., Shao G., Homewood K. P., Is there a future for semiconducting silicides, *Microelectronic Engineering* **50** (2000) pp. 223-235.
8. van Ek J., Turchi P. E. A., Sterne P. A., Fe, Ru, and Os disilicides: Electronic structure of ordered compounds, *Phys. Rev. B* **54** (1996) pp. 7897-7908.
9. Mantl S., *Nucl. Instrum. & Methods B* **84** (1994) 127.
10. Sharpe J., Chen Y. L., Gwilliam R. M., Kewell A., Mckinty C. N., Lourenço M., Shao G., Homewood K. P., Reeson K. J., Ion beam synthesised Ru_2Si_3 , *Appl. Phys. Lett.* **79** (1999) pp. 1282-1283.
11. Miglio L., Meregalli V., Theory of FeSi_2 direct gap semiconductor on Si (100), *J. Vac. Sci. & Technol. B* **16** (1998) pp. 1604-1609.
12. Eppenga R., *J. Appl. Phys.* **68** (1990) 3027.
13. Christensen N. E., *Phys. Rev. B* **42** (1990) 7148.
14. Radermacher R., Shuppen A., Mantl S. *Solid State Electron.* **37** (1994).
15. Katsumata H., Makita Y., Kobayashi N., Shibata H., Hasegawa M., Aksenov I., Kimura S., Obara A., Uekusa S., *J. Appl. Phys.* **80** (1996) 5995.
16. Dimitriadis C. A., Werner J. A., Logothetidis S., Stutzmann M., Weber J., Nesper R., *J. Appl. Phys.* **68** (1990) 1726.
17. Lefki H., Muret P., Cherief N., Cinti R. C., *J. Appl. Phys.* **69** (1991) 35.
18. Reeson K. J., Finney M. S., Harry M. N., Hutchinson S. V., Tan Y. S., Leong D., Bearda T., Yang Z., Curello G., Homewood K. P., Gwilliam R. M., Sealy B. J. Electrical, optical & materials properties of ion beam synthesised (IBS) FeSi_2 , *Nucl. Instrum. & Methods B* **106** (1995) pp. 364-371.
19. Lourenço M. A., Kewell A. K., Gwilliam R. M., Butler T. M., Kirkby K. J., Homewood K. P., Electrical and electronic characterization of iron disilicide light emitting devices, *Accepted Nucl. Instrum. & Methods B*.
20. Leong D., Harry M., Reeson K. J., Homewood K. P., On the origin of the 1.5 μm luminescence in ion beam synthesized beta- FeSi_2 , *Appl. Phys. Lett.* **68** (1996) pp. 1649-1650.
21. Yang Z., Homewood K. P., Finney M. S., Harry M. A., Reeson K. J., Optical-absorption study of ion-beam synthesized polycrystalline semiconducting FeSi_2 , *J. Appl. Phys.* **78** (1995) pp. 1958-1963.
22. Reeson K. J., Hunt T. D., Homewood K. P., Teon S. W., Gwilliam R. M., Sealy B. J., Optical properties and phase transformations in α and β - FeSi_2 layers, *Nucl. Instrum. & Methods B* **84** (1994) pp. 168-171.
23. Sauer R., Weber J., Stoltz J., Weber E. R., Kuster K. H., Alexander H., *Appl. Phys. A* **36** (1985).

24. Leong D., Harry M., Reeson K. J., Homewood K., A silicon/iron-disilicide light-emitting diode operating at a wavelength of 1.5 μm , *Nature* **387** (1997) pp. 686-688.
25. Miglio L., Meregalli V., Interpretation of the infrared spectra of $\beta\text{-FeSi}_2$ by molecular dynamic simulations, *Mat. Res. Soc. Symp. Proc.* **402** (1996) pp. 367-372.
26. Lourenço M. A., Butler T. M., Kewell A. K., Gwilliam R. M., Kirkby K. J., Homewood K. P., Electroluminescence of $\beta\text{-FeSi}_2$ light emitting devices, submitted to *J. Appl. Phys.*
27. Suemasu T., Negishi Y., Takakura K., Hasegawa F., Room temperature electroluminescence from a Si-based light emitting diode with $\beta\text{-FeSi}_2$ active region, *Jpn. J. Appl. Phys.* **39** (2000).
28. TRIM.

PHYSICS OF MULTIWALLED CARBON NANOTUBES

C. SCHÖNENBERGER

*Institute of Physics, University of Basel
Klingelbergstrasse 82, CH-4056 Basel, Switzerland*

E-mail: Christian.Schoenenberger@unibas.ch

L. FORRÓ

*Institute de Génie Atomique, École Polytechnique Fédérale de Lausanne
CH-1015 Lausanne, Switzerland*

E-mail: Laszlo.Forró@epfl.ch

We briefly review a couple of highlights in multiwalled carbon nanotube research. We will emphasize mechanical properties of nanotubes in general and then focus on electrical properties of multiwalled nanotubes in particular.

1 Introduction

Imagine being a tailor in the nanoworld with the task of tailoring a robust drinkstraw for a virus. You might come to the idea of taking a sheet of graphite (known as graphene), cutting out a long slice which is then rolled up and stitched together to form a carbon tube. These single-wall carbon nanotubes are reality, but rather than sewing the borders together, Nature forms these tubes seamless with a typical diameter of 1-2 nm. Sumio Iijima at NEC Fundamental Research Laboratory in Tsukuba discovered these giant molecules in 1991 when he studied the soot created by a direct-current arc discharge between carbon electrodes with high resolution transmission electron microscopy. What Iijima found were nanotubes consisting of several concentrically arranged single-wall carbon tubes nested into each other like a russian doll (see Fig. 1). These multishell nanotubes have outer diameters typically in the range of 10-50 nm and are now referred to as multiwalled carbon nanotubes (MWNTs). Later, Single-wall nanotubes (SWNTs) were discovered too and an efficient method for their production was found by Thomas Ebbesen and coworkers, also at NEC. Today, nanotubes can also efficiently be grown by catalytic decomposition of a carbon containing reaction gas. For a review, see [1].

Carbon nanotubes can be viewed as giant buckyball molecules, also called fullerenes. The basic buckyball is a 60 carbon atom soccer ball. If sliced into two halves, a ring of 10 atoms can be added to get a rugby-ball. Repeating this will

result in cylindrical molecules capped by half a buckyball at both ends. This is in fact also true for well ordered MWNTs, for which all shells are capped. Multishell fullerenes are also known and called carbon onions. A multiwall nanotube is therefore a cylindrical onion or a carbon leek. Apart from these different shapes, the physics of carbon nanotubes depends on the direction of the tube axis relative to the lattice of the graphite sheet. There are many possible choices to roll a slice of graphene into a seamless cylinder. If bent into a nanotube, the hexagons may spiral around the cylinder. Depending on this "chirality" carbon nanotubes can be metals with high electrical conductivity, or semiconductors with a relatively large band gap.

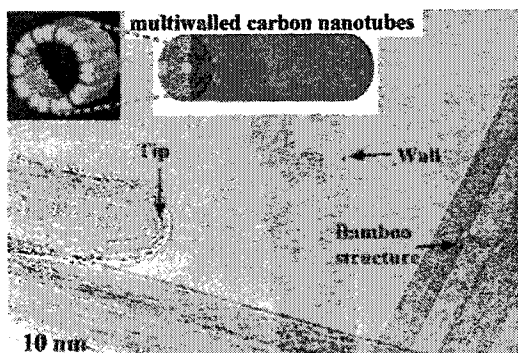


Figure 1. Multiwall carbon nanotubes are composed of a set of single-wall tubes concentrically stacked into each other with a typical outer diameter of 20 nm. It is clearly seen in the high-resolution transmission-electron microscopy image of a well ordered MWNT grown in an arc-discharge.

Nanotubes have other remarkable properties: they are robust, very stiff with record elastic modulus, but at the same time not brittle at all. They can snap from one shape to the other if strongly compressed to finally resume their original perfect straightness if relaxed. These mechanical properties can, for example, be exploited for reinforcement, for nanomanipulators (tweezers) and for high-resolution scanning probe tips. Being composed of carbon only, nanotubes have a low specific weight, too. Furthermore, carbon nanotubes are hollow tubes and may be used in the future as nanopencils in which the capillary is used to deliver "ink" on the nanometer scale.

2 Mechanical properties

In 1996 Treacy, Ebbesen and Gibson from NEC Princeton and the University of Illinois studied MWNTs, which were rigidly supported on one side, in a transmission-electron microscope (TEM) [2]. The free ends of the nanotubes appeared considerably blurred. These nanotube levers do vibrate, stimulated by thermal excitations, causing the observed blurring. From the measured vibration

amplitude, an exceptionally high elastic modulus (Young's modulus E) of order $E = 1$ Tpa was derived. For a comparison, steel has a five times lower modulus. It is now known that for tubes with a radius larger than 1 nm, the Young's modulus should approach a value of 1.25 Tpa. This is true both for MWNT and SWNT because the modulus is mainly determined by intra-shell carbon bonds. This value has recently been confirmed. Charles Lieber and coworkers from Harvard University used a scanning-force microscope (SFM) to intentionally bend nanotubes which were dispersed on a substrate and mechanically fixed on one side [3]. The scanning-force microscope not only allowed to image and manipulate the tubes, but could also be employed to measure the force needed to bend the tubes. Similar values for E were obtained.

Another technique to explore the bending stiffness was developed by Jean-Paul Salvetat and coworkers from the EPFL in Switzerland [4]. It involves depositing nanotubes from a suspension onto well-polished alumina ultrafiltration membranes with a pore size of about 200 nm. By chance, carbon nanotubes occasionally span the pores. The deflection of these supported tubes is then deduced from atomic-force microscopy (AFM) images operating at various normal loading force. The measured deflection is inversely proportional to the Young's modulus. Salvetat and coworkers compared the modulus of MWNTs grown by arc-discharge and catalytic decomposition of hydrocarbons. E is found to be approximately 1 Tpa for the former, while for the catalytic ones a much lower – by one to two orders of magnitudes – modulus was found. This result demonstrates that only highly ordered and well graphitized nanotubes have a stiffness comparable to graphite.

Charles Lieber and coworkers not only studied the elastic behaviour of nanotubes for small deflections (linear regime) but went on to explore what happens for large deformations. They also compared carbon nanotubes with nanorods made of silicon-carbide (SiC), another very strong material. There was a surprise: whereas the continuous bending of the carbide nanorods ultimately led to fracture, MWNTs could be bent over large angles without fracturing. Instead buckling was observed. This elastic buckling has now been confirmed in several experiments, in which the nanotubes are either bent or axially compressed. Axial compression without any relaxation is possible up to the limit, which has been calculated by the great mathematician Euler. Beyond this Euler-limit the initially straight tube or rod will flip into a curved form. If this experiment is performed with a drinking straw at constant load, the straw will suddenly develop kinks. These kinks are not elastic, but rather plastic deformations. The kinks remain if the load is removed. The carbon nanotubes are magic in this respect. If the force exceeds the bending strength, or the Euler limit if axially loaded, they first bend over surprisingly large angles, start to ripple and buckle to finally develop kinks as well. The amazing thing is that all these deformations are elastic and disappear completely if the load is removed. If combined with energy-absorbing materials, these mechanical properties of nanotubes may be useful not only for cars but also for light bulletproof vests and earthquake-resistant buildings. For additional reading, see [5-7].

The high strength of carbon nanotubes makes them promising candidates in reinforcement applications. There are many outstanding problems to be overcome before composite materials can be fabricated, which reflect the exceptional mechanical properties of the individual nanotubes. As well as optimizing the material properties of the individual tubes, the tubes must be bonded to a surrounding matrix in an efficient way to enable load transfer from the matrix to the tubes. In addition, efficient load bearing within the tubes themselves needs to be accomplished in such a way that shearing is prevented.

3 Electrical properties

Carbon nanotubes are giant molecular wires in which electrons can freely propagate, as in an ordinary metal. This strongly contrasts with conventional "conducting" polymers (like, for example, polythiophene) where the electrons localize. These molecules are actually insulators and become conductors only if heavily doped. Furthermore, conducting polymers have considerably shorter conjugation lengths. Each carbon atom of the graphene honeycomb lattice has four valence electrons of which three are strongly bound to neighbours giving graphene its in-plane rigidity. The fourth electron is delocalized and shared by all the atoms allowing for electrons to conduct. However, it turns out that a single sheet of graphite (graphene) is electronically a hybrid: it is neither a semiconductor, nor a metal. Graphene is a semimetal or a "zero-gap" semiconductor. This peculiarity renders the electronic states very sensitive to additional boundary conditions, as the periodic boundary condition along the circumference of a carbon nanotube.

A stationary electron wave can only develop, if the circumference of the tube is a multiple of the electron wavelength. This condition removes the peculiarity of graphene and turns nanotubes into either true metals or semiconductors [1]. For MWNTs one expects a more complicated and richer dependence, because of a possible additional electronic coupling between adjacent shells. For a review, see [8]. Combining different nanotubes and supplementing these with gate electrodes a large variety of electronic components ranging from wires, bipolar devices to field-effect transistors can be embodied in nanotubes. On the fundamental side, a perfect metallic nanotube is supposed to be a ballistic conductor. A ballistic conductor is the best (normal electron) conductor an engineer can dream of, only beaten by a superconductor. If an electron is injected from a contact into a ballistic wire with ideal contacts, the electron will end at the drain contact with certainty. There is no back-scattering in the wire, which is the source of intrinsic electric resistance and leads to Ohm's law. A defectless carbon nanotube is like an optical fibre with two propagating modes, which results in to an electrical conductance that is twice as large as the fundamental conductance unit G_0 ($G_0 = 2 e^2/h$). Note, that the resistance is not zero as it would be for a superconductor. But quite in contrast to classical resistors and to Ohm's law, the resistance is independent of the length of the wire.

In 1998 Walt de Heer and his colleagues from the Georgia Institute of Technology invented an ingenious way for measuring the electrical conductance of single MWNTs [7]. A macroscopic fibre of MWNTs was fixed on a manipulator which allowed to steer the fibre above a drop of liquid metal (for example mercury). Because individual MWNTs stick out from the fibre, a single MWNT can now easily be contacted by gently lowering the fibre into the conducting liquid. By dipping the nanotubes to different depths it is possible to determine the resistance per unit length, which should be zero in an ideal ballistic wire. This method of contacting a nanotube is very different to, for example, the structuring of metal electrodes to nanotubes using high-resolution sub-micron fabrication technology (an example is shown in Fig. 2).

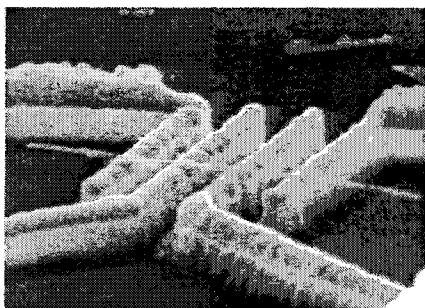


Figure 2. SEM image of a MWNT lying across four Au electrodes, which were fabricated by state-of-the-art electron-beam lithography prior to the deposition of the nanotube.

Reasonably low-ohmic contacts, both for MWNTs and SWNTs, were very difficult to achieve in previous experiments. It is important to emphasize that the quantized conductance can only be observed if ideal contacts are realized. These early experiments showed that MWNTs are far from being ballistic. In contrast, strong evidence was found that electrons scatter in nanotubes, so that transport is more appropriately characterized as diffusive. Taken these early experiments the results of de Heer and coworkers were very surprising. First, these researchers showed that all MWNTs had nearly the same conductance corresponding to one conductance quantum. Secondly, the length dependent resistance was found to be very low. These two results suggest that MWNTs are ballistic conductors, despite the many shells that may be expected to interact.

Because MWNTs consist of several concentrically arranged SWNTs, one would expect that MWNTs do not qualify as one-dimensional conductors. If adjacent carbon shells interact as in graphite, electrons may not be confined to one shell only. The results of de Heer and coworkers suggest however that the current mainly flows through the outermost shell only. Our own investigation has proven that this is indeed the case. In this respect, studying electric transport in MWNTs is somewhat similar to studying transport in a large diameter SWNT. The nanotube core solely acts as a mechanical support for the electrically active outermost shell.

Note, that is this is no longer true, if we would found a way to contact the bulk, or even were able to selectively address inner shells. MWNTs have certain specific advantages over SWNTs: their large diameter favour low-ohmic contacts, because of the larger contact area. Arc-discharge grown MWNTs do not contain magnetic impurities, which is important for spintronics, in which the spin of the electrons is used for magnetic-sensing or switching applications or even for computation. Their large diameter enables to investigate quantum-interference phenomena in magnetic field.

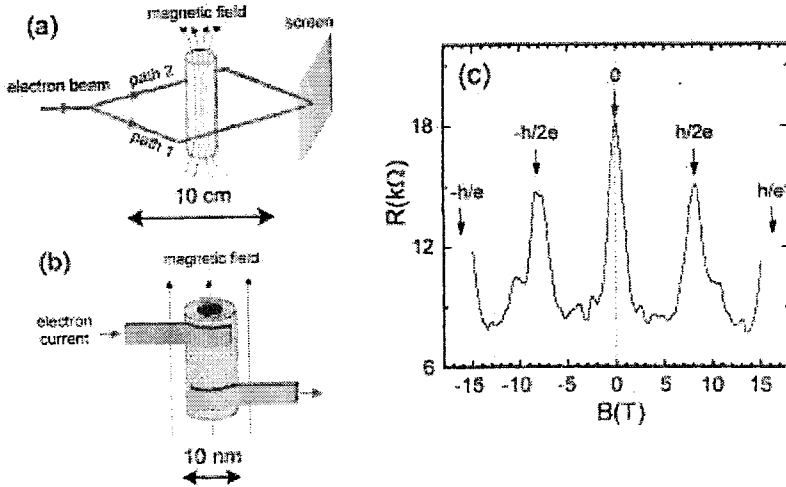


Figure 3. (a) Illustration of the Aharonov-Bohm (AB) effect. The flux through the solenoid changes the relative phase of the electron-waves in path 1 and path 2 of this two-beam electron interferometer. This affects the intensity modulation on the screen (the interference pattern). Similarly, the electron waves in a carbon nanotube are modified by the magnetic flux threading the interior of the tube (b). The change in interference pattern in (a) translates into a change of the electric resistance in (b). (c) shows the measured resistance R as a function of parallel magnetic field. The arrows point to multiple flux-quanta $h/2e$.

The most profound quantum-interference effect is the Aharonov-Bohm (AB) effect. The illustration in Fig. 3 shows what happens if an electron beam is split into two partial beams following different paths, but merge together on a screen on which the electron intensity is measured. One observes an intensity modulation in the form of a periodic stripe pattern. Such a pattern is called interference pattern. Its observation demonstrates that in this experiment a single electron does not choose either path but behaves as an extended wave which has amplitude on both paths simultaneously. The two paths form a closed loop threaded by a magnetic flux. Though electrons need never come in "contact" with the magnetic field, the interference pattern changes periodically with the flux with a period given by the magnetic-flux quantum $\Phi_0 = h/e$. This is the Aharonov-Bohm effect.

Now imaging a carbon nanotube (a single wall for simplicity) placed in a magnetic field parallel to the tube axis (Fig. 3(b)). Since nanotubes are cylindrical

conductors the electrons that propagate on the cylinder can circle around the tube in either the clockwise or counter-clockwise direction. These two "paths" interfere, as in the example discussed before, resulting in a periodic modulation of the electrical resistance with magnetic flux through the hollow. In this case the period is half the flux-quantum. This effect is relatively robust and can even be observed if transport in nanotube is diffusive. For an ideal ballistic nanotube, a much more dramatic effect is expected. Whether a nanotube is a semiconductor or a metal depends only on the relative phase of the wavefunction around the tube circumference. Since the magnetic flux changes the phase, a metallic nanotube should continuously evolve into a semiconducting one and vice versa.

We have placed single electrically contacted MWNTs in a parallel field and studied both the temperature and flux dependence of the electrical resistance [10]. Fig. 3(c) displays the main result. There is a resistance peak at zero magnetic field. This peak reappears at approximately ± 8.5 Tesla, although with reduced amplitude. If this increase is caused by the AB effect, resistance peaks should appear equidistantly. The additional resistance increase at the highest field of 15 Tesla agrees with this expectation. The magnetic field at the peak position can be related to the diameter of the nanotube, which turns out to be equal to the geometric outer diameter of the nanotube measured independently. This demonstrates unambiguously, that the electric current is carried by the outermost tube only. We would like to mention here, that in order to observe the first peak in a similar experiment with SWNTs would one require a magnetic field of 1000 Tesla because of the small tube radius. The peak separation in Fig. 3(c) corresponds to half ϕ_0 suggesting that transport is not ballistic in our MWNTs. If it were ballistic a much larger effect should have been observed, since the metallic nanotube would be turned into a semiconductor with a gap much larger than the measuring temperature.

This and other magneto-resistance measurements have allowed to deduce the scattering length and the length dependent resistance. We found that transport is diffusive. A large variation in scattering length have been deduced, ranging from 3 nm (very diffusive) to 100 nm (quasi-ballistic, i.e. intermediate between diffusive and ballistic). That the observed metal-to-semiconductor transition has not been observed is a puzzle which needs to be solved, as we have to find an explanation for the large variation in scattering length, from near infinity (de Heer et al.) to a couple of nanometers. Although transport in our MWNTs is best characterized as diffusive, large electric currents (up to 1 mA) can be passed through the nanotubes, demonstrating that the electrons couple only weakly, if at all, to the lattice. All magnetoresistance measurements can very well be understood in the Fermi liquid framework assuming two-dimensional diffusive transport. However, recent measurements of the tunneling DOS in MWNTs have revealed anomalies quite similar to feature seen in SWNT which were assigned to Luttinger liquid behaviour.

Maybe the most exciting (and controversial) recent finding is the claim for *intrinsic superconductivity* in ropes of SWNTs. A transition to a seemingly superconducting state below ~ 0.4 K has been observed by Yu. Kasumov,

H. Bouchiat and coworkers in nanotubes contacted by a special laser tool enabling to achieve very low-ohmic contacts [11].

4 Outlook

Carbon nanotubes have shown a wealth of phenomena. Some results we firmly understand already, others are controversial today. Nanotubes are great molecules and good conductors with a wide range of interesting properties useful for applications. The future for nanotube looks very bright: Nanotubes are interesting model systems for fundamental studies of one-dimensional systems, but they are equally well (or even more) attractive to applied researchers and industries due to the large variety of potential applications.

References

1. For a review see: Dekker C., Carbon nanotubes as molecular quantum wires, *Physics Today* (1999) 22.
2. Treacy M. M. J., Ebbesen T. W., Gibson J. M., *Nature* **381** (1996) 678.
3. Wong E. W., Sheehan P. E., Lieber C., *Science* **277** (1997) 1971.
4. Salvetat J.-P., Kulik A. J., Bonard J.-M., Briggs G. A. D., Stöckli T., Méténier K., Bonnamy S., Béguin F., Burnham N. A., Forró L. *Adv. Mater.* **11** (1999) 161.
5. Falvo M. R., Clary G. J., Taylor R. M., Chi V., Brooks Jr. F. P., Washburn S., Superfine R., *Nature* **389** (1997) 582.
6. Yu M.-F., Lourie O., Dyer M. J., Moloni K., Kelly T. F., Ruoff R. S., *Science* **287** (2000) 637.
7. Poncharal P., Wang Z. L., Urgate D., de Heer W., *Science* **283** (1999) 1513.
8. Schönenberger C., Bachtold A., Strunk C., Salvetat J.-P., Forró L., *Appl. Phys. A* **69** (1999) 283.
9. Frank S., Poncharal P., Wang Z. L. de Herr W. A., Carbon Nanotube Quantum Resistors, *Science* **280** (1998) 1744.
10. Bachtold A., Strunk C., Salvetat J.-P., Bonard J.-M., Forró L., Nussbaumer T., Schönenberger C., *Nature* **397** (1999) 673.
11. Kociak M., Kasumov A. Yu., Guéron S., Reulet B., Khodos I. I., Gorbатов Yu. B., Volkov V. T., Vaccarini L., Bouchiat H., *Superconductivity in ropes of single-walled carbon nanotubes*, preprint.

INVITED

ULTRA THIN C₆₀-BASED FILMS: MOLECULAR ARRANGEMENT AND ELECTRONIC STATES

C. CEPEK

Laboratorio Nazionale TASC-INFM

AREA Science Park, Strada Statale 14, Km. 163 Basovizza, I-34012, Trieste, Italy

E-mail: cepek@sci.area.trieste.it

M. SANCROTTI

Laboratorio Nazionale TASC-INFM

AREA Science Park, Strada Statale 14, Km. 163 Basovizza, I-34012, Trieste, Italy

and Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore

Via dei Musei 41, I-25121 Brescia, Italy

E-mail: sancrotti@sci.area.trieste.it

We comparatively analyze three distinct C₆₀-based superstructures grown on Ag(100), Si(111)-(7×7), and Ge(111)-c(2×8) as to their molecular arrangement and electronic structure. The basic elements characterizing covalent vs. ionic bond of the buckyballs with the substrate are discussed. In particular, the attention is focused onto STM images, photoemission spectra of the C 1s core level and valence band states.

1 Introduction

In the last years, the possibility of producing, controlling, and manipulating atomic/molecular blocks at the nano meter scale opened a new era, where novel artificially structured materials with tailored properties can be fabricated. C₆₀ molecules, with their quasi-spherical shape of ≈ 7 Å diameter, may be considered as perfect nano particles and elemental blocks for nano materials. In this connection, the formation of chemically stable C₆₀ monolayer films on many kinds of surfaces has become a subject of great interest for the scientific community [1]. Actually fullerene thin films are proving useful to encapsulate fragile surface reconstruction and/or are functioning as templates for the formation of novel structures [1-3]. This soccer-ball shaped molecule differs significantly from the elemental or simple molecular adsorbates because of its three dimensional character along with the strong modulation of the valence charge distribution over the molecular cage [4]. This unique electronic structure leads to several possible interaction mechanisms between C₆₀ and the host surface, while the geometrical constraints imposed by the three dimensional cage allow only a few carbon atoms per molecule to be in contact with the substrate [5,6]. Moreover, the C₆₀ molecules present the very important

property that it is possible to tailor their electronic structure from semiconducting to metallic and even to superconducting states just by doping [4,7].

In this paper we examine and compare the main features of the C_{60} adsorption on low Miller index surfaces when the bond between the C_{60} molecules and the substrate is characterized by a predominant ionic or covalent bond. We have chosen as a template for the ionic bond the metallic surface Ag(001), in which the C_{60} molecules have been found to be in the charge state $\approx 2e$, and for the covalent bond the semiconductor surfaces Ge(111)- $c(2 \times 8)$ and Si(111)-(7 $\times$ 7).

All the systems have been studied by means of high-resolution photoemission spectroscopy. The chosen surfaces are characterized by a low photoemission cross section in the energy region up to the C_{60} (HOMO-1) (highest occupied molecular orbital) derived bands, in order to single out better the fullerene derived structures due to the bond with the substrate.

2 Experimental

The measurements have been performed in ultra high vacuum conditions with a base pressure of about 1×10^{-10} mbar.

Sample cleanliness and order have been checked by means of photoemission and low energy electron diffraction (LEED). The procedures for the preparation of the clean and ordered Ag(001), Ge(111)- $c(2 \times 8)$, and Si(111)-(7 $\times$ 7) surfaces have been reported elsewhere [8-10].

Pure C_{60} powder (99.9 %) has been sublimated from a tantalum crucible, using an evaporation rate of ≈ 0.2 ML/min. The C_{60} multilayer film, characterized by a well ordered hexagonal LEED pattern, has been grown on the ordered C_{60} ML on Ag(001) (see below) keeping the substrate at ≈ 450 K. The C_{60} monolayer (ML) on the different substrates have been obtained by evaporating the C_{60} molecules on the surfaces kept at a temperature which enables us to obtain a single compact layer of molecules. In particular the annealing temperature was 670 K for the growth on Ag(001) and Ge(111)- $c(2 \times 8)$, and 800 K on Si(111)-(7 $\times$ 7). Using these preparation procedures the molecules form a quasi-hexagonal close packed single layer superstructure on all the substrates, as shown in Fig. 1. Due to the higher mobility of the C_{60} molecules, the ML on Ag(001) and Ge(111) present long range order, showing, respectively, a $c(6 \times 4)$ LEED pattern, where the C_{60} - C_{60} distance is $\approx 10.4 \text{ \AA}$ [11] and a $3\sqrt{3} \times 3\sqrt{3} R30^\circ$ LEED pattern, where four inequivalent molecules are present and where the C_{60} - C_{60} distance is $\approx 10.0 \text{ \AA}$, like in solid C_{60} [9].

The C 1s core level spectra have been obtained at room temperature exciting the electrons by synchrotron radiation with photon energy of ≈ 430 eV in normal emission geometry. In particular, the C 1s spectra of the C_{60} ML on Ag(001) and Si(111) and of the multilayer have been measured at the VUV beamline of the synchrotron radiation facility ELETTRA (Trieste, Italy), achieving an overall energy resolution of ≈ 110 meV on the C_{60} multilayer and on the ML on Ag(001)

and of ≈ 65 meV on the ML on Si(111) (from [13]). The C 1s on Ge(111) has been measured at the SU8 French-Spanish beamline of the LURE synchrotron radiation facility (Orsay, France), achieving in this case an overall energy resolution of ≈ 100 meV.

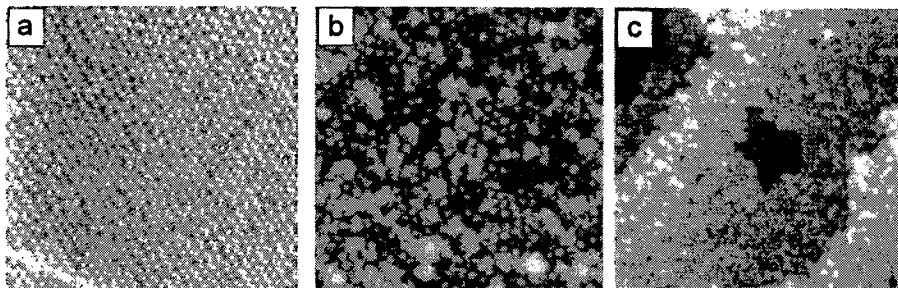


Figure 1. STM images of the single layer of C_{60} molecules adsorbed on: a) Ag(001) surface at 670 K, forming the $c(6 \times 4)$ superstructure [14], b) Si(111)-(7 $\times$ 7) surface at ≈ 670 K [15] and c) Ge(111)- $c(2 \times 8)$ at 670 K, forming the $3\sqrt{3} \times 3\sqrt{3}R30^\circ$ superstructure [16]. In the figures each ball is relative to a single C_{60} molecule.

The valence band photoemission spectra have been measured in normal emission geometry, using a conventional ultra-violet He discharge lamp ($h\nu=21.2$ eV), obtaining an overall energy resolution of ≈ 100 meV.

3 Results and discussion

As already mentioned in the previous section, most of the C_{60} over-layers form quasi-hexagonal superstructures upon adsorption on almost all the substrates already investigated in the literature. The interaction with the substrate may be thermally activated and the annealing at an appropriate temperature may induce also different reconstructions of the substrate [4]. The strength of the bond may reduce the mobility of the C_{60} molecules, as is the case of buckyball adsorption on silicon surfaces. Moreover, the C_{60} molecules may not present long-range order, but in any case the quasi-hexagonal geometry is locally preserved. This can be easily seen also in the herein presented systems, as shown in the scanning tunneling microscopy (STM) images of Fig. 1.

The adsorption of the fullerene molecules on Ag(100) at ≈ 450 K is characterized by charge transfer (≈ 2 electrons) from the substrate to the molecules and by long range order, with a rather sharp $c(6 \times 4)$ LEED pattern, in which the distance between the molecules is ≈ 10.42 Å [11,16]. The STM images (Fig. 1(a)) of the annealed ML exhibit dim and bright molecules, which are arranged in a sort of zig-zag pattern. On the contrary, we note that the images of the ML grown and measured at $T < 300$ K show only one kind of molecules [17], indicating that annealing at $T > 300$ K changes the interaction of the molecules with the surface and/or may induce substrate local reconstruction.

The origin of the STM contrast is still a matter of debate. One of the most probably correct explanations is that the bright/dim contrast seen in STM is due to orientationally ordered and disordered molecules. In fact, it has been recently demonstrated by means of X-ray photoelectron diffraction (XPD) that on this system $\approx 60\%$ of the molecules present orientational order on the surface and they are arranged into two inequivalent molecular orientations [18]. Preferred molecular orientations have been observed in many other metallic substrates [19,20], and in general the molecular orientation seems to be driven by both molecule-substrate and molecule-molecule interaction. We note that the observation of preferred orientations is an indication that the interaction with the substrate is characterized by a bond stronger than the one between the molecules in solid C_{60} . In fact, in solid C_{60} the molecules are mainly bounded with van der Waals forces and the molecules are almost free rotators at $T > 260\text{ K}$ [4]. In the system where the interaction with the substrate is stronger, the molecule present several molecular orientations, like for example on Si substrates. In this case the bond is that strong that the molecules do not desorb from the surface neither upon annealing at $T \approx 1000\text{ K}$, but react with Si atoms to form thin SiC layers [10,14,21].

Based on the data published so far in the literature it results that the bond between the adsorbed C_{60} molecules and metal substrates is primarily ionic for low work function metals (e.g. noble metals) whereas covalency dominates for high work function metals. Elemental semiconductors such as Si and Ge are characterized by covalent bonds with the C_{60} cages, these bonds being activated by temperature [22].

The donation of electrons to the buckyballs occurs via progressive filling of the pristine C_{60} LUMO (lower unoccupied molecular orbital) derived orbitals. This effect has been extensively studied in bulk exo-fullerides via doping with alkali and rare-earth atoms. Interestingly, the progressive doping allows one to move from the semiconducting state of pure solid C_{60} to metallic phases up to insulating phases. In particular systems the donation of three electrons to the C_{60} cages corresponds to the formation of a superconductor with relatively high critical temperature.

Electronic charge transfer to the buckyballs and parallel partial filling of the LUMO orbital can be also obtained when C_{60} molecules are deposited onto selected substrates. Beside this, the interaction between the adsorbed molecules and the substrate is sometime dominated by the formation of covalent bonds between C-atoms directly facing the substrate. Another issue of fundamental importance is whether and how the adsorption properties are affected by temperature. In principle, one might expect to drive the surface mobility of the ad-molecules as a function of temperature as well as possible disruption processes of the C_{60} cages at high temperatures.

One of the most powerful experimental techniques, which enables one to understand the kind of interaction between C_{60} molecules and different substrates, is photoemission spectroscopy. Fig. 2 shows the photoemission valence band of the C_{60} molecules adsorbed on the Ag(100), Ge(111)- $c(2 \times 8)$ and Si(111)- (7×7) surfaces

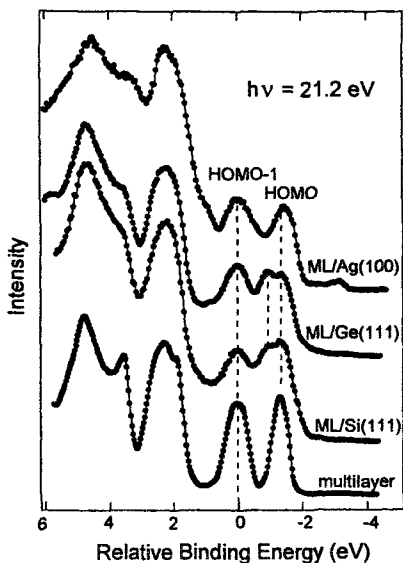


Figure 2. Valence band photoemission spectra of, a C_{60} multilayer and 1-ML C_{60} on Si(111)-(7 $\times$ 7), Ge(111)-c(2 $\times$ 8), and Ag(100) surfaces. All the spectra have been measured in normal emission geometry by using a conventional He discharge ultra-violet lamp. All the energies are referred to the HOMO-1 peak of the C_{60} multilayer.

compared with a C_{60} multilayer film. All the chosen substrates are characterized by a low photoemission cross section compared to the C 2p one in the energy region up to the C_{60} HOMO-1 derived bands. Consequently all the structures up to the C_{60} HOMO-1 peak of the MLs spectra are related only to the C_{60} overlayer. The C_{60} multilayer spectrum is the typical photoemission spectrum of this compound. It is characterized by a sequence of structures strictly related to the C_{60} -related molecular orbitals. In particular we note the HOMO-1 and HOMO structures. On a binding energy scale, the energy location of these structures changes remarkably as the substrate and the coverage thickness are varied. This reflects the differing charge states and chemical environment local to the C_{60} cages. In Fig. 2, the energy scale of all the spectra is referred to the HOMO-1 peak of the multilayer

film in order to better discriminate the differences due to the bond with different surfaces. It is worthwhile noticing several important features in these spectra.

1. All the C_{60} features at binding energy lower than the HOMO-1 peak maintain the same relative energy from it, even if the fine structures at ≈ 1.8 eV and ≈ 3.7 eV of the C_{60} multilayer get broader.
2. The ML grown on Ag(100) shows an extra emission close by the Fermi level. This is related to the partial filling of the C_{60} LUMO orbital as a result of electron charge transfer from the silver substrate to the adsorbed buckyballs.
3. The HOMO peak in the ML adsorbed on Si(111) and Ge(111) is split into two components which are at the same relative binding energy from the HOMO-1 and present different weight depending on the substrate. The component at lower binding energy has the same relative position with respect to the HOMO-1 as in the case of C_{60} multilayer.
4. The energy difference between the HOMO-1 and HOMO in the case of the adsorption on Ag(100) is higher than the C_{60} multilayer, while on Ge(111) and Si(111) is lower.

From the above points, it is clear that the structures most affected from the bond are the C_{60} LUMO and HOMO. The appearance of a peak at lower binding energy of the C_{60} HOMO is a clear indication of a partially filling of the LUMO, and indicates that charge transfer from the substrate to the buckyballs takes place. In the case of strong interaction with a prevalent covalent bond, and without charge transfer, the C_{60} LUMO appears split into two components. The component at higher binding energy reflects the number of the carbon atoms bonded with the substrate [9,10].

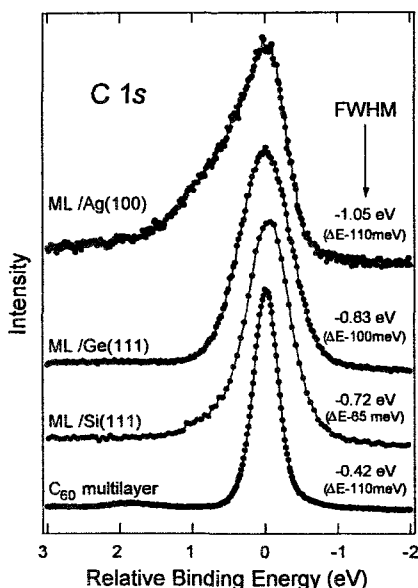


Figure 3. C 1s photoemission spectra of a C_{60} multilayer and 1-ML C_{60} on Si(111)-(7x7), Ge(111)-c(2x8), and Ag(100) surfaces.

In general, C_{60} chemisorption at metal and semiconductor surfaces induces a chemical shift towards lower BE and an asymmetric line shape in the C 1s emission [4]. The size of this chemical shift is rather the same in both cases of bonds, i.e. ionic vs. covalent. Significantly, the asymmetry of the C 1s line shape is definitely more pronounced when charge transfer governs the substrate-to- C_{60} cage bond. This corresponds to the fact that the additional electronic charge redistributes all over the buckyball producing a wide variety of chemically distinct C atoms. In contrast, in the case of covalency, the bond is primarily local to the few C atoms directly facing the substrate. These features can be easily seen in Fig. 3 where the C 1s photoemission line of a C_{60} multilayer and of three 1-ML C_{60} chemisorbed on different substrates are shown.

4 Conclusions

We have compared different C_{60} monolayer systems which are characterized by prevalent covalent or ionic bond by means of C 1s core levels and valence band photoemission spectroscopy. The typical fingerprint of charge transfer from the substrate to the fullerenes in the valence band spectra is the appearance of the C_{60} LUMO orbital. The covalent bond on the Ge(111)-c(2x8) and Si(111)-7x7 surfaces is characterized by the splitting of the C_{60} HOMO into two component appearing with different weight, which indicates a different number of C atoms bonded with

the substrate at two growing temperatures investigated (670 K and 800 K, respectively). The asymmetry of the C 1s line shape is more pronounced when charge transfer governs the bond between the C₆₀ balls and the substrate.

5 Acknowledgements

This work has been financed by the INFM via the CLASS advanced research project and by the CNR via the FILINCLUBE project. We are profoundly grateful to M. Pedio, A. Goldoni, M. C. Asensio, M. De Seta, J. Avila, E. Magnano, A. Pesci, L. Ferrari, U. Valbusa, C. Boragno, G. Costantini and L. Giovanelli who contributed to the realization of this work.

References

1. Dresselhaus M. S., Dresselhaus G., Eklund P. C., *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996); Klyachko D., Chen D. M., *J. Vac. Sci. Technol. B* **15** (1997) 1295.
2. Hong H., McMahon W. E., Zschack P., Lin D.-S., Aburano R. D., Chen H., Chiang T.-C., *Appl. Phys. Lett.* **61** (1992) 3127.
3. Ma Y.-R., Moriarty P., Upward M. D., Beton P. H., *Surf. Sci.* **397** (1998) 421.
4. Weaver J., Poirier D. M., In *Solid State Physics: Advances in Research and Applications*, ed. by Ehrenreich H., Spaepen F. (Academic Press, Boston, 1994); Rudolf P. In *Proceeding of the Xth International Winterschool on Electronic Properties of Novel Materials*, ed. by Kuzmany H., Fink J., Hehring H., Roth S. (World Scientific, Singapore, 1996).
5. Ohno T. R., Chen Y., Harvey S. E., Kroll G. H., Weaver J. H., Haufler R. E., Smalley R. E., *Phys. Rev. B* **44** (1991) 13747.
6. Maxwell A. J., Brühwiler P. A., Arvanitis D., Hasselstöm J., Johansson M. K. J., Mårtensson N., *Phys. Rev. B* **57** (1998) 7312.
7. Schön J. H., Kloc Ch., Batlogg B., *Nature* **408** (2000) 549.
8. Magnano E., Vandré S., Cepek C., Goldoni A., Laine A. D., Currò G., Santaniello A., Sancrotti M., *Surf. Sci.* **377-379** (1997) 1066.
9. Goldoni A., Cepek C., De Seta M., Avila J., Asensio M. C., Sancrotti M., *Phys. Rev. B* **61** (2000) 10411.
10. Cepek C., Schiavuta P., Sancrotti M., Pedio M., *Phys. Rev. B* **60** (1999) 2068.
11. Goldoni A., Cepek C., Magnano E., Laine A. D., Sancrotti M., *Phys. Rev. B* **58** (1998) 2228.
12. Pesci A., Ferrari L., Comicioli C., Pedio M., Cepek C., Schiavuta P., Pivetta M., Sancrotti M., *Surf. Sci.* **454-456** (2000) 832.
13. Cepek C., Giovanelli L., Sancrotti M., Costantini G., Boragno C., Valbusa U., *Surf. Sci.* **454-456** (2000) 766.

14. Suto S., Sakamoto K., Kondo D., Wakita T., Kimura A., Kakizaki A., Hu C W., Kasuya A., *Surf. Sci.* **438** (1999) 242.
15. Hu H., Chen D. M., Creager W. N., *Phys. Rev. B* **50** (1994) 8454.
16. Cepek C., Sancrotti M., Greber T., Osterwalder J., *Surf. Sci.* **454-456** (2000) 467.
17. Giudice E., Magnano E., Rusponi S., Boragno C., Valbusa U., *Surf. Sci.* **405** (1998) L561; Costantini G., Rusponi S., Giudice E., Boragno C., Valbusa U., *Carbon* **37** (1999) 727.
18. Cepek C., Fasel R., Sancrotti M., Greber T., Osterwalder J., *Phys. Rev. B* (15 March 2001)
19. Fasel R., Aebi P., Agostino R. G., Naumovic D., Osterwalder J., Santaniello A., Schlapbach L., *Phys. Rev. Lett.* **76** (1996) 4733; Fasel R., Agostino R. G., Aebi P., Schlapbach L., *Phys. Rev. B* **60** (1999) 4517.
20. Maruyama Y., Ohno K., Kawazoe Y., *Phys. Rev. B* **52** (1995) 2070; Johansson M. K. J., Maxwell A. J., Gray S. M., Brühwiler P. A., Mancini D. C., Johansson L. S. O., Mårtensson N., *Phys. Rev. B* **54** (1996) 13472; Johansson M. K. J., Maxwell A. J., Gray S. M., Brühwiler P. A., Mancini D. C., Johansson L. S. O., *Surf. Sci.* **397** (1998) 314; Hou J. G., Jinlong Y., Haiqian W., Qunxiang L., Changgan Z., Hai L., Wang B., Chen D. M., Qingshi Z., *Phys. Rev. Lett.* **83** (1999) 3001.
21. Chen D., Sarid D., *Phys. Rev. B* **49** (1994) 7612; Chen D., Sarid D., *Surf. Sci.* **318** (1994) 74; Li Y. Z., Chander M., Patrin J. C., Weaver J. H., Chibante L. P. F., Smalley R. E., *Phys. Rev. B* **45** (1992) 13837.
22. Maxwell A. J., Brühwiler P. A., Arvanitis D., Hasselstöm J., Johansson M. K. J., Mårtensson N., *Phys. Rev. B* **57** (1998) 7312.

ON A POSSIBILITY OF THE MOTT TRANSITION IN A QUANTUM DOT ENSEMBLE

A. I. BIBIK

*Institute of Molecular and Atomic Physics, National Academy of Sciences
F. Skaryna Pr. 70, 220072 Minsk, Belarus*

E-mail: bibik@imaph.bas-net.by

The possibility of the dielectric-metal transition (Mott transition) as a result of increase of charge carriers concentration in the conductivity band of an ensemble of close-packed monodispersed nanocrystals is mathematically proved. The results of statistical analysis providing of occurrence of metal conductivity in a system of ordered and disordered semiconductor nanocrystals depending on their concentration, size and electron effective mass are reported.

The progress of engineering and technique of experiment with nanocrystals (NCs) gives an opportunity of comprehensive study [1,2] of NCs and mesoscopic structures on their basis. The opportunities of synthesis of spatially organized NC ensembles [3-5] pose a problem of quantitative description of optical and electronic properties of NCs at transition from individual ones to the associates. In this paper we shall try to answer a question: whether there are the conditions at which the metal conductivity in the system of monodisperse close-packed semiconductor NCs exists.

We are to consider the dielectric-metal transition in NC system by analogy with its occurrence for an impurity lattice in heavily doped semiconductors [6]. To outline an analogy between NCs and impurity centers we should treat the monodisperse close-packed NC system as a set of identical potential spherical quantum wells (QWs) of radius R , taking into account that an electron passes from valence band of NC to its conductivity band as a result of photon absorption and such electron can move within NC similarly to motion of a particle in QW.

Thus, we consider the system in which there is one electron in each QW. In this QW one state can be populated with two electrons with different spins whose interaction energy U_0 will be about e^2/a , where a is a Bohr radius. If the interaction energy is small compared with the width of a forbidden band of an ensemble QWs, the reorganization of wave functions involved into electron interaction will be insignificant. In the case of distant-located QW the size of the allowed band is exponentially small and much less than U_0 . In this case in each QW there will be two electronic levels. The electron energy is equal to E_0 (or E_0+U_0 depending on whether there is one more electron in this QW) (Fig. 1). At a final value of QW lattice period both levels extend to bands. The quantity of states in each of those bands is equal to number of QWs. The bottom band turns out to be filled and the top one is empty. Thus, if width of a band is less than U_0 , our system will be an

dielectric. At reduction of distance L between QW at some point L_0 the width of a forbidden band will become equal to zero and there is the dielectric-metal transition, which is usually called Mott transition [7].

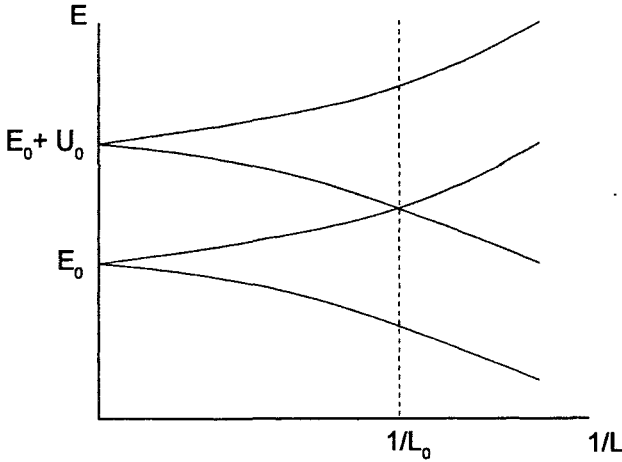


Figure 1. The origin of electronic bands depending on period L of a QW lattice. To the left of point $1/L_0$ there is the dielectric state and to the right – the metal one.

As a criterion of the Mott transition we shall accept the distance between QWs at which the expansion of electronic levels exceeds the energy of electron-electron repulsion in one QW. The problem is being reduced to the determination of parameter L_0 , which in the case of an ordered arrangement of QWs is determined as a crystal lattice period corresponding to the dielectric-metal transition, and in the case of a chaotic arrangement of QWs it is equal to an average distance $1/C^{1/3}$ between QWs, where C is QW concentration. For simplicity, as a crystal lattice we shall consider the simple cubic lattice with period L , and the chaotic arrangement of QW we shall set through deviation with the Gaussian distribution of their coordinates from cubic lattice nodes (not exceeding a lattice half-period).

We describe the QW by the hydrogen-like potential, which in atomic units will be written as follows:

$$U(r) = -\frac{ZE_a}{r}, \quad (1)$$

where E_a is the atomic energy unit (≈ 27.21 eV), coordinate r is measured in Bohr radii $a = \frac{a_0}{m^*/m_0}$, where a_0 is atomic length unit (≈ 0.5292 Å), m_0 is the electron rest mass. Parameter Z is a function of effective electron mass m^* , ϵ and NC radius R

and can be found from condition of equality the ground electronic state energy in our case and that in the spherical QW model with finite depth [8].

The widening of subbands as a result of interaction of QWs may be estimated by considering two adjacent QWs as a hydrogen molecule. We shall estimate width of a forbidden band by analogy to the difference of energies of electrons with different spins in the ground state of He atom. Thus we arrive to the definition of Mott transition criterion as:

$$U_0 \leq E_t - E_s, \quad (2)$$

where E_t and E_s correspond to triplet and singlet electronic energy states of the hydrogen-like molecule, and the repulsion energy of two electrons according to [9] is:

$$U_0 \cong \frac{5Z}{8} - 0.315311 + \frac{0.01707}{Z} \quad (3)$$

The calculations were made for an ensemble of QWs ordered in to the simple cubic lattice with the period L (Fig. 2(a)), and also for an ensemble of QWs, chaotically located in cells of the cubic lattice with the side L (Fig. 2(b)).

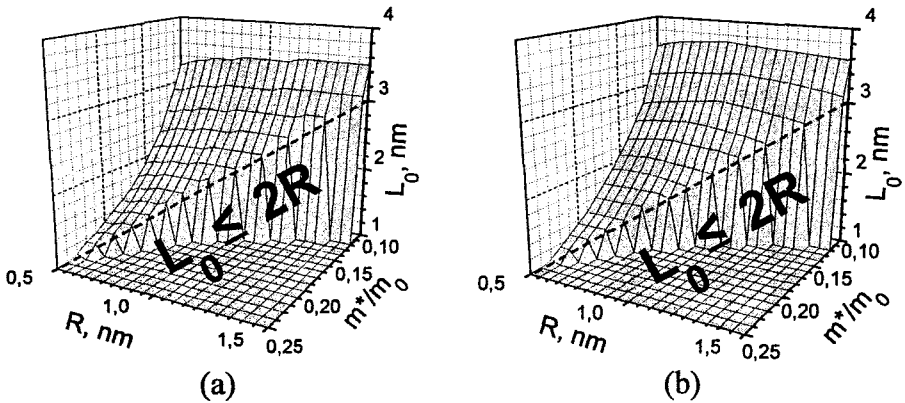


Figure 2. Dependence of average distance L_0 between NCs of radius R at which the Mott transition is possible on NC radius and electron effective mass m^* . (a) - simple cubic lattice, (b) - disordered NC ensemble.

For a disordered QWs ensemble the fulfillment of (2) for fragments of the system consisting of an arbitrarily chosen QW and six its nearest neighbours was checked. The statistical analysis was made for 500 fragments of the NC ensemble for the full set of parameters $\{L, R, m^*\}$. For the disordered system, it was taken into account that according to the theory, channels of metal conductivity can be formed when the condition (2) is performed for 25 % of QWs.

In conclusion, the Mott transition is possible only for systems of close-packed NCs with small size and small electron effective mass. We can offer as a test object,

for example, films of close-packed CdSe NCs whose electronic and optical properties were studied before [4,5].

The author thanks S. V. Gaponenko for the proposed problem and N. A. Poklonski for fruitful discussions.

References

1. Gaponenko S. V., *Optical properties of semiconductor nanocrystals* (Cambridge University Press, Cambridge, 1998).
2. Alivisatos A. P., *Science* **271** (1996) 933.
3. Vossmeier T., Reck G., Katsikas L., Haupt E. T. K., Schulz B., Weller H., *Science* **267** (1995) 1476.
4. Murray C. B., Kagan C. R., Bawendi M. G., *Science* **270** (1995) 1335.
5. Kagan C. R., Murray C. B., Nirmal M., Bawendi M. G., *Phys. Rev. Lett.* **76** (1996) 1517.
6. Shklovskii B. I., Efros A. L., *Electron Properties of Doped Semiconductors* (Nauka, Moscow, 1979; Springer, Berlin, 1982).
7. Mott N. F., *Metal-Insulator Transitions* (London, Taylor and Francis, 1974).
8. Nosaka Y., *J. Phys. Chem.* **95** (1991) 5054.
9. Bethe H., Salpeter E., *Quantum mechanics of one- and two- electron atoms* (Springer, Berlin, 1957).

SCREENING OF EXTRA POINT CHARGE IN A FEW PARTICLE COULOMB SYSTEM

N. A. POKLONSKI, A. I. SIAGLO, S. A. VYRKO, V. V. MITIANOK

*Belarusian State University
220050 Minsk, Belarus*

E-mail: poklonski@phys.bsu.unibel.by

Analytical description of Coulomb field screening generated by extra point charge, placed in the center of semiconductor ball (nanocluster) with a limited number of donors and acceptors is given in the continual approximation. The screening occurs due to hopping of electrons between donors. Our calculations of the electrostatic potential is compared with the results of the Monte-Carlo numerical modeling at zero temperature.

The study of the “superatoms” [1], nanocrystals [2] in solid matrices and condensation in Coulomb systems [3] is actual for many applications [4]. In [5] the hopping exchange of electrons between metallic nanoballs in the dielectric matrix has been studied. At the same time hops of electrons between point defects in nanoclusters structure are also possible.

Let us calculate the electrostatic potential of extra single charge q placed in the center of a spherical nanocluster, when the matrix and cluster are made of the same material with permittivity ϵ . For this purpose we consider isotropic crystalline insulator, containing $v_d = v_0 + v_{+1}$ donors in the charge states (0) and (+1) as well as $v_a = v_d / 2 = v_{-1}$ acceptors in the charge state (-1) inside the electroneutral spherical region of radius R at temperature $T = 0$. The donor concentration is $N_d = 3v_d / 4\pi R^3$. The compensation degree of donors by acceptors is $K = v_a / v_d = 0.5$. We believe that the electrons hop between the donors without escape into the matrix.

Let the extra charge $q = \pm e$ be inserted in the center of the electroneutral ball (nanocluster) of radius $R = (3v_d / 4\pi N_d)^{1/3}$, where $e > 0$ is the electron charge. Eventually point charge q will be enclosed with spherically symmetric cloud of charges, screening it. This screening cloud consists of electrons, hopping between donors in charge states (0) and (+1), and immovable acceptors in charge state (-1). The Poisson equation for electrostatic potential $\phi_s(r)$ in the nanocluster is [6,7]:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi_s}{dr} \right) = -\frac{q}{\epsilon} \delta(r) - \frac{\rho_s(r)}{\epsilon}, \quad (1)$$

where $\rho_s(r) = \rho_s[\phi_s(r)]$ is the density of the screening charge; r is the distance from the central extra charge q ; $\delta(r)$ is the three-dimensional Dirac delta function.

The donor energy level $E_d > 0$ in the nanocluster and the Fermi level E_F are counted off from the bottom of c-band of the virgin crystalline matrix. We assume that the distribution of donor energy levels E_d relatively to average value $\bar{E}_d > 0$ has the normal density $g_d = (\sqrt{2\pi}W)^{-1} \exp[-(E_d - \bar{E}_d)^2 / 2W^2]$ where W is the root-mean-square fluctuation of the potential energy of charged donor. At the compensation degree $K = 0.5$ we obtained [8]:

$$W \approx 1.64 \frac{e^2}{4\pi\epsilon} \left(\frac{4\pi N_d}{3} \right)^{1/3}, \quad (2)$$

where the Poisson distribution for distances between point defects in the electroneutral nanocluster is assumed and the Coulomb interaction of donor in the charge state (+1) only with the nearest ion is taken into account.

At low temperature ($T \rightarrow 0$) the donor states with energies $E_d > |E_F|$ in electrically neutral nanocluster are filled by electrons, but states with $E_d < |E_F|$ are empty. In the absence of extra charge, the concentration of positively charged donors is $N_{+1} = N_d/2 = N_a$. When there is extra charge q , the local concentration of the positively charged donors is [7]:

$$N_{+1}(\varphi_s) = N_d \int_{E_F + \bar{E}_d + e\varphi_s}^{+\infty} g_d d(E_d - \bar{E}_d) = \frac{N_d}{2} \left[1 - \operatorname{erf} \left(\frac{E_F + \bar{E}_d + e\varphi_s}{W\sqrt{2}} \right) \right], \quad (3)$$

where $\varphi_s(r)$ is the potential inside the nanocluster; $E_F = -\bar{E}_d$ for $v_d = 2v_a$.

From (3) we get the screening charge density distribution: $\rho_s(\varphi_s) = e[N_{+1}(\varphi_s) - N_{+1}]$. When $e|\varphi_s| \ll W$ charge density ρ_s linearly depends on the potential φ_s . If a nanocluster contains 300 structural defects ($v_d = 200$, $v_a = 100$) at $r = l \approx 0.554(1.5N_d)^{-1/3}$, where l is the mean distance from the screened charge q to the nearest defect, the condition $e|\varphi_s(r)| < W$, taking into account (2), is fulfilled even for Coulomb potential $\varphi(r) = q/4\pi\epsilon r$. So, (1) in linear approximation becomes [7-9]:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\varphi_s}{dr} \right) = -\frac{q}{\epsilon} \delta(r) + \lambda^{-2} \varphi_s(r), \quad (4)$$

where the screening length λ of the electrostatic field (after Debye-Hückel) is [8]:

$$\lambda^{-2} = \frac{-1}{\epsilon} \left(\frac{d\rho_s}{d\varphi_s} \right)_{\varphi_s=0} = \frac{-e^2}{\epsilon} \frac{\partial N_{+1}}{\partial E_F} = \frac{e^2 N_d}{\epsilon W \sqrt{2\pi}}. \quad (5)$$

The general solution of (4) is [6,10]:

$$\varphi_s(r) = \frac{q}{4\pi\epsilon r} [A_- \exp(-r/\lambda) + A_+ \exp(r/\lambda)], \quad (6)$$

where A_- and A_+ are defined from the boundary conditions; $\lambda \approx 1.17 R / v_d^{1/3}$.

Let us use the condition for electric field $E(r) = -\partial\varphi_s/\partial r$ at $r = l \approx 0.78 R / v_d^{1/3}$ and $r = R$. Since at $r \leq l$ as well as at $r \geq R$ the field generated by the "central" charge q is pure Coulomb, so the boundary conditions are: $E(l) = q/4\pi\epsilon l^2$; $E(R) = q/4\pi\epsilon R^2$. Therefore we get from (6):

$$A_{\mp} = \frac{\lambda[(1 \mp \lambda)\exp(\pm 1/\lambda) - (R \mp \lambda)\exp(\pm R/\lambda)]}{(R + \lambda)(1 - \lambda)\exp[(1 - R)/\lambda] - (R - \lambda)(1 + \lambda)\exp[(R - 1)/\lambda]}.$$

When we add to the constant potential $\varphi_s(r)$

$$\varphi_0 = \frac{q}{4\pi\epsilon R} [1 - A_- \exp(-R/\lambda) - A_+ \exp(R/\lambda)], \quad (7)$$

then the electrostatic potential of the nanocluster with extra point charge q is equal to $q/4\pi\epsilon R$ at $r = R$, i. e. it coincides with the potential of a point charge.

In Fig. 1 the potential $\varphi_t = \varphi_s + \varphi_0$ of extra point charge in the center of the ball containing $v_d = 200$ donors and $v_a = 100$ acceptors calculated with (6) and (7) is shown. Note that the numerical solution of (1) for potential φ_s with the screening charge density $\rho_s(r) = e[N_+(\varphi_s) - N_+]$ from (3) coincides with the potential calculated with (5) and (6). For the solution (6) the electroneutrality condition is fulfilled:

$$4\pi \int_1^R \rho_s(r) r^2 dr = -\frac{4\pi\epsilon R}{\lambda^2} \int_1^R \varphi_s(r) r^2 dr = 0.$$

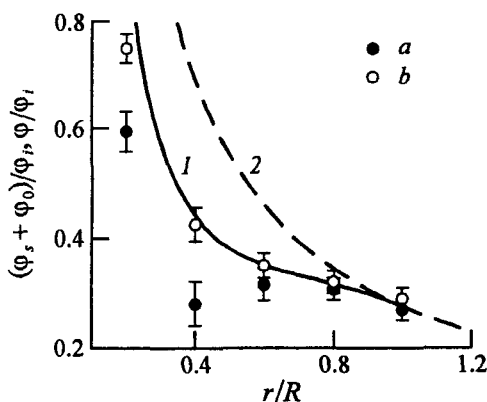


Figure 1. The electrostatic potential (in units of $\varphi_t = eN_d^{1/3}/4\pi\epsilon$) of the point charge $q = e$, placed in the center of the ball of radius R ; the curve 1 represents $\varphi_s + \varphi_0$ from (6,7); 2 is pure Coulomb potential $\varphi = e/4\pi\epsilon r$; the points a , b are values of $\frac{\varphi_{MC}}{|\varphi_{MC}|}$, $\frac{|\varphi_{MC}|}{|\varphi_{MC}|}$, respectively, obtained in [11] by the Monte-Carlo method.

In [11] ground state of donors ($v_d = 200$) and acceptors ($v_a = 100$) in the ball of radius R with charge $q = +e$ in the center and without charge at $T \rightarrow 0$ was obtained by the Monte-Carlo (MC) method. The initial distribution of charges was random. Each next distribution of the charges was different from previous one by carrying one electron from neutral donor to positively charged one. Only transitions decreasing the system energy were taken into account. After 1200 transitions of electrons the distribution of the positive charged donor states in the ball, corresponding to the case when the electrostatic energy of the system is minimal, was found. Then electrostatic potential $\varphi_{MC}(r)$ was defined as the difference between potentials of the ball with charge $q = e$ in the center and the neutral ball. The potential was calculated for 6 points inside the ball, where the sphere of radius r intersects Cartesian coordinate axes. This procedure was repeated for 60 coordinates of donors and acceptors. Averaging of $\varphi_{MC}(r)$ and $|\varphi_{MC}(r)|$ was done finally.

Fig. 1 shows the value of average $\overline{\varphi_{MC}(r)}$ and average module $\overline{|\varphi_{MC}(r)|}$ values in units of $\varphi_i = eN_d^{1/3}/4\pi\epsilon$ (points a and b) calculated in [11] in comparison with the potential $\varphi_s(r) + \varphi_0$. Unfortunately, values of root-mean-square potential $[\overline{\varphi_{MC}^2(r)}]^{1/2}$, which should be larger than $\overline{\varphi_{MC}}$ and $\overline{|\varphi_{MC}|}$, were not given in [11]. At the same time formula (6) for the potential $\varphi_s(r)$ was obtained in the linear approximation (4), when $|\varphi_s(r)| = [\overline{\varphi_s^2(r)}]^{1/2}$.

References

1. Andryushin E. A., Silin A. P., *Fiz. Tverd. Tela* **33** (1991) 211. (in Russian).
2. Gaponenko S. V., *Optical properties of semiconductor nanocrystals*, (Cambridge, Cambridge University Press, 1998).
3. Likal'ter A. A., *Uspekhi Fizicheskikh Nauk* **170** (2000) 831. (in Russian).
4. *Nanotechnology*, ed. by G. Timp (N.Y., Springer-Verlag, 1999).
5. Baskin É. M., Entin M. V., *JETP Letters* **70** (1999) 520.
6. Wermer J., *Potential Theory* (Berlin, Springer-Verlag, 1974).
7. Poklonski N. A., Stelmakh V. F., *Phys. Stat. Sol. (b)* **117** (1983) 93.
8. Poklonski N. A., Siaglo A. I., *Phys. Solid State* **40** (1998) 132.
9. Ishihara A., *Electron liquids*, 2nd. ed. (Berlin, Springer-Verlag, 1998).
10. Farlow S. J. *An Introduction to Differential Equations and Their Applications*. (N.Y., McGraw-Hill, Inc., 1994).
11. Baranovskii S. D., Shklovskii B. I., Efros A. L., *Zhurn. Eksper. Teor. Fiz.* **87** (1984) 1793. (in Russian).

A SUPERLATTICE WITH RESONANT STATES IN A UNIT CELL: THE BAND STRUCTURE AND ELECTRON TRANSITIONS

A. V. DMITRIEV¹, R. KEIPER², V. V. MAKEYEV¹

¹*The Department of Physics, Moscow State University
119899 Moscow, Russia*

²*Institute of Physics, Humboldt—University Berlin
Invalidenstr. 110, 10115 Berlin, Germany*

E-mail: dmitriev@lt.phys.msu.su

We study theoretically the electron spectrum and infrared transitions in a superlattice with a unit cell allowing resonant carrier states. The dispersion relation and the band structure of such a system is found. The dipole matrix element and optical absorption strength for inter-subband carrier infrared transitions are calculated for the first time.

1 System

We consider a superlattice with the unit cell allowing quasi-localized (resonant) carrier states. For example, if the well is surrounded by two additional semi-transparent barriers on the top of the main barriers, the quasi-local states may appear above the main barrier top. We consider a simplified model of this kind of potential (see Fig. 1):

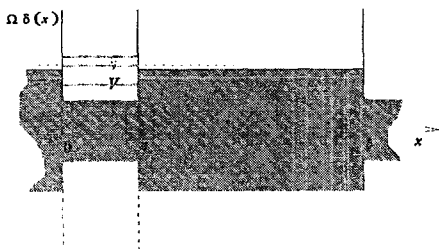


Figure 1. The considered model potential. Several lower subbands are marked. Shadow area corresponds to the energy gap.

$$U(x) = \begin{cases} -V, & 0 < x < a \\ 0, & a < x < b \end{cases} + \Omega[\delta(x) + \delta(x-a)], \quad (1)$$

where x is the growth direction of the superlattice, a and b are the well width and the structure period, respectively, V is the well depth. δ -like barriers on the well's edges represent a simplified approximation of additional real barriers of finite width and height that would surround every well. Parameter Ω corresponds to the reverse tunnel transparency of the real barrier. The main barriers of width $(b-a)$ separate the wells.

2 Motivation

Quasi-localised states may be present in artificially prepared heterostructures, e.g. in two-barrier quantum well systems. We have shown earlier [1] that in their presence the absorption coefficient significantly increases in the frequency range corresponding to intraband transitions into the resonant state. In the cited paper [1] we discussed a single quantum well system. However, arrays of quantum wells or superlattices are normally used for experimental purposes and practical applications. Therefore it is reasonable to consider a periodic structure composed of quantum wells with resonant states.

3 Theory

We consider one non-degenerate band of a semiconductor superlattice where every cell is described within the effective mass approximation by a one-dimensional model potential (1).

The envelope wave functions of electrons may be represented as

$$\Psi(x) = \begin{cases} A_1 e^{iqx} + A_2 e^{-iqx}, & 0 < x < a \\ B_1 e^{ikx} + B_2 e^{-ikx}, & a < x < b \end{cases}; \quad \Psi(x+b) = e^{ikb} \Psi(x), \quad (2)$$

where $q = (1/\hbar)\sqrt{2m(E+V)}$, $k = (1/\hbar)\sqrt{2mE}$, E is the particle energy counted from the top of the main barrier, m is the effective mass, kb is the phase shift of the envelope function, resulting from one lattice period displacement along the growth direction. Ignoring the changes in the effective mass across the superlattice layers, we obtain a conventional boundary condition at the left-hand border of the well ($x=0$):

$$\Psi(x)\Big|_{0-}^{0+} = 0, \quad \frac{d}{dx} \ln \Psi(x)\Big|_{0-}^{0+} = \Omega. \quad (3)$$

Having written similar boundary conditions for the right-hand border ($x=a$), we come to a homogeneous system of equations defining the coefficients in (2). A non-zero solution of this system exists only if the system determinant is zero, hence we come to the dispersion relation. Solving the corresponding equation numerically, we found the miniband structure of the superlattice.

4 Discussion

Fig. 2 depicts the envelope wave functions of several adjacent subbands. The lower plot represents a wave function belonging to the lowest subband. This band originates from the well's ground state. Naturally, electronic density concentrates within the well's limits.

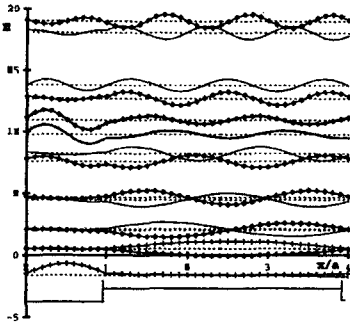


Figure 2. The subband structure of the superlattice for $b/a = 4$ and $V = 1.47$. The energy unit is $\hbar^2/ma^2$. The subband edges are marked by horizontal dotted lines. Solid curves represent the envelope functions at the band edges, of which the states with $k=0$ are marked with rhombuses. Two thick solid curves denote the functions of the 'resonant' subband. The unit cell potential is shown below.

The rest of the wave functions in Fig. 2 correspond to positive energy values. Most of them have electronic density concentrated just outside the wells. We can roughly infer that these functions originate from electronic states residing over the barriers. These functions have different parities according to the well centre on the opposite edges of each subband.

In the subband with the energy close to the resonant value the functions do not obey the latter rule. Here electronic density is large within the well limits, and the envelope functions have the same parity at the band edges. Henceforth, we can expect $p_n(k)$, the dipole matrix element of optical transition between these two bands, to be anomalously large because of strong overlap between the wave functions in the two bands. Then the absorption coefficient would also increase.

Figs. 3, 4 depict the dependence of $|p_n|^2$ on the energy of the final electron state at two different values of superlattice period. The transition matrix element goes up

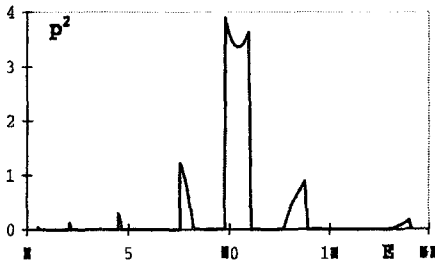


Figure 3. The momentum matrix element squared measured in $\hbar^2/a^2$ for the same system as in Fig. 2 ($b/a = 4$). The energy unit is $\hbar^2/(ma^2)$.

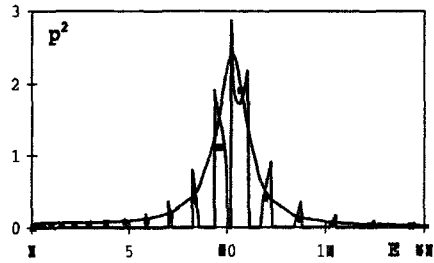


Figure 4. The same dependence as in Fig. 3, but for thicker main barriers: $b/a = 10$. The well depth $V = 1.47$. Full squares show the ratio of $\langle |p_n|^2 \rangle / (E_n - E_{n-1})$ for the superlattice. The smooth curve represents $|p_n|^2 \rho$ in a single quantum well according to [1].

in a number of subbands in the area of resonance. Absorption reaches maximum at one edge and drops almost to zero at the other edge of the subband. This is true for all subbands except the resonant one. While before the resonance absorption monotonously goes down from the lower edge to the upper one. After the

resonance, the picture becomes reversed. Matching the picture with Fig. 2, we see that when absorption is maximum, the final wave function has 'proper' parity, i.e. the opposite to the parity of the ground state. In the resonant the band parity is 'proper' at both band edges, and band absorption spectrum has different shape.

It is interesting to observe the superlattice energy spectrum variation over the parameter region where the resonant state of the well leaves one subband and enters another. Fig. 5 illustrates this process at the variation of the well depth.

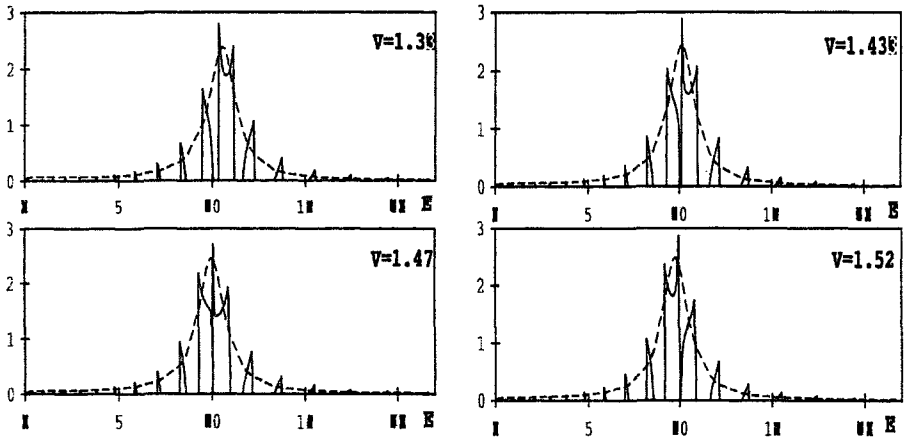


Figure 5. The change of $|p_n|^2$ for the system of Fig. 4 under variation of V , the well depth. (a) $V = 1.33$, (b) 1.433, (c) 1.47, (d) 1.52.

Using the momentum matrix element data shown above we have also calculated in a rather straightforward way such directly measurable physical quantity of interest as the absorption strength due to the electronic transition from the ground subband to a higher one.

References

1. Dmitriev A. V., Keiper R., Makeyev V. V., *Semiconductor Sci. Technol.* 11 (1996) 1791.

DISPERSION OF GUIDED PLASMON-POLARITONS IN A PLANAR BRAGG MICRORESONATOR WITH TWO-DIMENSIONAL ELECTRON SYSTEM

V. V. POPOV, G. M. THYMBALOV

*Saratov Division of the Institute of Radio Engineering and Electronics
Russian Academy of Sciences
410019 Saratov, Russia*

E-mail: popov@ire.san.ru

We present results of theoretical investigation of the plasmon-polaritons formed due to the interaction of two-dimensional plasmons in a planar Bragg microresonator with guided modes of dielectric substrate slab. The guided plasmon-polaritons may be taken up for development of controllable guided wave frequency filters and modulators in the far-infrared.

Recently, the interaction of dipole electron excitations in two-dimensional (2D) electron system with electromagnetic (EM) cavity modes has been extensively studied. Particularly, the exciton-phonon coupling in cavity-embedded quantum wells has received the bulk of attention. The exciton-phonon coupling results in the anticrossing between excitonic states and the resonator photon modes which gives birth to the cavity-polaritons [1-4]. The cited papers are devoted to radiative exciton-polaritons. Radiative polariton dispersion has been measured in angle-resolved photoluminescence experiments [3,4].

Plasma oscillations in 2D electron systems are nonradiative electron dipole excitations [5]. Hence, they can not couple to EM radiation through one-phonon absorption or emission processes. To couple 2D plasmons to EM wave a lateral diffraction grating with periodicity $L \ll \lambda$, where λ is the EM wavelength, is formed on the top surface of the structure [5]. The grating couples transverse EM wave to longitudinal plasma oscillations with in-plane wavevector $k_{\parallel} = 2\pi m/L$ ($m=1,2,3\dots$). In fact, such grating makes up an open Bragg resonator for 2D plasma oscillations. The theory of EM emission from 2D (magneto)plasmons in semiconductor heterostructure with planar metal grating was developed in [6,7].

In a plane-parallel dielectric substrate slab the EM field confinement takes place only for guided modes with in-plane wavevectors from the interval $\omega/c < k_{\parallel} < \omega(\epsilon_s)^{1/2}/c$, where c is the light velocity, ω is the angular frequency of EM wave, ϵ_s is the dielectric constant of the substrate medium. Here we present a theoretical investigation of the plasmon-polaritons formed due to the interaction of 2D plasmons in a planar Bragg resonator with guided modes of dielectric substrate slab. The structure under consideration involves a plane-parallel dielectric slab of thickness d (semi-insulating GaAs in actual semiconductor heterostructures) with 2D electron system on one of its faces. Planar grating with periodicity L consists of

perfectly conducting strips of width w and it is separated from 2D electron system by dielectric interlayer of thickness δ (wide band gap semiconductor AlGaAs). The in-plane wavevector of polariton excitations studied in this paper is aligned with the direction of the grating periodicity.

The theoretical results given below were obtained through a straightforward extension of our previously published theory [6] to the case of finite thickness of the structure substrate. Similarly to [6,7], 2D electron plasma is described by conductivity σ_{2D} in the local approximation (the Drude model):

$$\sigma_{2D} = \frac{e^2 N_{2D} \tau}{m^* (1 + i\omega\tau)},$$

where N_{2D} is the density of electrons of charge e and effective mass m^* , τ is the phenomenological relaxation time. We assume that the substrate dielectric constant ϵ_s is equal to that of interlayer ϵ_i and the both take the value of 12.8 which is characteristic for GaAs. This assumption is virtually justified because of rather small difference of ϵ_s from ϵ_i in actual heterostructures GaAs/AlGaAs as well as because of the small interlayer thickness (which is found to be of the order of plasmon wavelength) as compared to that of the substrate. The other parameters used in the calculations are also typical for GaAs/AlGaAs heterostructures.

Fig. 1 shows the region of interaction of the fundamental (lowest in the frequency) 2D plasma oscillations with the fundamental EM guided TM-mode of the dielectric substrate slab for the case where there is no electron scattering in the

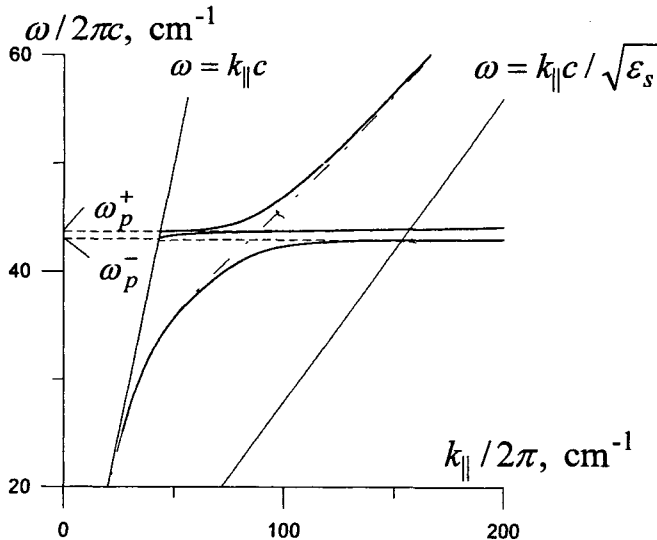


Figure 1. Guided plasmon-polariton dispersion in the structure with parameters $N_{2D}=6.7 \times 10^{11} \text{ cm}^{-2}$, $d=3.5 \times 10^{-3} \text{ cm}$, $\delta=8 \times 10^{-6} \text{ cm}$, $L=8.7 \times 10^{-5} \text{ cm}$, $w/L=0.9$.

2D system ($1/\tau = 0$). Dispersion of the fundamental *TM*-mode is given by the dash-dotted line. Dashed lines are dispersions of the fundamental 2D plasma oscillations in a planar Bragg resonator on the substrate of infinite thickness.

It is known [6] that 2D plasma oscillations with wavevector $k_{\parallel} = 0$, which corresponds to the center of the first Brillouin zone in the reduced band scheme of the Bragg resonator, split up into doublets. One mode in a doublet is radiative while the other is nonradiative. The frequencies of the fundamental nonradiative and radiative modes are denoted in Fig. 1 as ω_b^+ and ω_b^- , respectively. The electric fields of different plasma oscillations in the doublet have symmetry of different parities in relation to the centers of the grating slits. The nonradiative mode possesses nodes of the longitudinal electric field at the centers of the grating slits while the radiative one exhibits antinodes of that there.

For $k_{\parallel} \neq 0$ a plasmon electric field amplitude distribution does not possess the symmetry with a definite parity in relation to the centers of the grating slits. Therefore, strictly speaking, the both plasma oscillations in the doublet experience radiative damping when their wavevector values fall into the interval $0 < k_{\parallel} < \omega/c$. However, the radiative damping of "nonradiative" mode remains several orders of magnitude weaker than that of the "radiative" one since the inequality $\omega/c \ll 2\pi/L$ is fulfilled. For the same reason, the plasma modes practically conserve definite parities of the symmetry of the electric field amplitude distributions in the interval of $k_{\parallel}$ shown in the figure.

All modes become nonradiative in the region of the dispersion plane to the right from the light line $\omega = k_{\parallel}c$. In the sector between the light lines $\omega = k_{\parallel}c$ and $\omega = k_{\parallel}c/(\epsilon_s)^{1/2}$, the confinement of EM field in the transverse direction arises from the total internal reflection of EM wave in the plane-parallel dielectric substrate slab. The electric fields of the guided modes decay with distance from the structure faces whereas inside the substrate a transverse standing wave is formed. When $k_{\parallel} > \omega c(\epsilon_s)^{1/2}/c$, there are only nonradiative 2D plasma oscillations with the electric fields decaying from 2D electron system survive in the structure.

One can see from Fig. 1 that well away from the interaction region the polariton dispersion merges into the dispersion of an uncoupled plasma or EM mode. In the interaction region the EM guided mode demonstrates the anticrossing with the plasma doublet. As the wavevector increases the lowermost polariton mode transforms from photonlike into plasmonlike mode. On the contrary, the uppermost polariton mode transforms from plasmonlike into photonlike mode. The third mode retains its plasma character at any wavevector value. But the parity of symmetry of the electric field amplitude distribution for this mode is reversed with increasing $k_{\parallel}$.

The calculations carried out with the electron relaxation in 2D system taken into account have shown that guided polariton attenuation may be as great as 50 dB/ λ at plasma resonance while it is under 0.5 dB/ λ away from the resonance. This offers possibilities for development of controllable guided wave frequency filters and modulators in the far-infrared EM wave range.

This work was supported by the Russian Foundation for Basic Research through grant 00-02-16440.

References

1. Savona V., Hradil Z., Quattropiani A., Schwendimann P., *Phys. Rev. B* **49** (1994) 8774.
2. Jorda S., *Phys. Rev. B* **51** (1995) 10185.
3. Houdre R., Gibernon J. L., Pelladini P. et al., *Phys. Rev. B* **52** (1995) 7810.
4. Tartakovskii A. I., Kulakovskii V. D., Forchel A., Reithmaier J. P., *Phys. Rev. B* **57** (1998) 6807.
5. Chaplik A. V., *Sur. Sci. Rep.* **5** (1985) 289.
6. Matov O. R., Polischuk O. V., Popov V. V., *Int. J. Infrared and Millimeter Waves* **14** (1993) 1445.
7. Matov O. R., Meshkov O. F., Polischuk O. V., Popov V. V., *JETP* **82** (1996) 471.

OPTICAL PROPERTIES OF FRACTAL CANTOR-LIKE MULTILAYER NANOSTRUCTURES

K. S. SANDOMIRSKI, S. V. GAPONENKO

*Institute of Molecular and Atomic Physics, National Academy of Sciences
220072 Minsk, Belarus*

S. V. ZHUKOVSKY, A. V. LAVRINENKO

*Physics Department, Belarusian State University
220080 Minsk, Belarus*

Optical properties of fractal Cantor-like multilayer structures are investigated theoretically and experimentally. The structures are shown to exhibit distinct optical properties, such as existence of band gaps and sharp resonances (peaks) in transmission spectra. Connection between the stack geometry and optical properties is found, namely spectral scalability and sequential splitting.

1 Introduction

Multilayer dielectric structures have been a subject of thorough investigation in recent years due to their distinctive optical properties and wide applications in various devices, from ordinary dielectric mirrors and high-Q optical cavities to spontaneous emission control and omnidirectional reflectors [1].

Both periodic (one-dimensional photonic crystals, 1D PC) and random multilayer stacks have been under study for quite a long time, and their properties seem to be generally understood. Nowadays, the focus of research is shifting towards a new, distinct class of media, which are non-periodic but deterministic. Such media include substitutional stacks (e.g. Fibonacci, Thue-Morse, and others) and fractal structures (Cantor and Koch multilayers). This paper deals with the latter ones, namely, Cantor-like structures.

2 Cantor-like multilayers

Cantor-like structures are fractal non-periodic multilayers generated according to an algorithm similar to that of Cantor set construction [2]. Any Cantor multilayer is characterized by two fundamental parameters, the *generator* $G=3, 5, 7 \dots$ and the *number of generations* $N=1, 2, 3 \dots$. Sample structures are shown in Fig. 1, and the algorithm of stack construction can be easily understood therefrom.

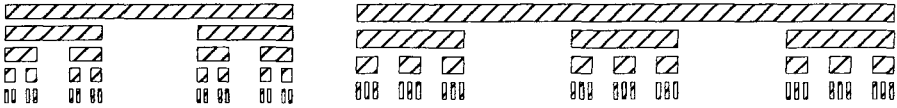


Figure 1. Cantor-like multilayers for $G=3$ (left) and $G=5$ (right) for several successive generations.

As we see, a Cantor multilayer consists of G^N layers. It is known that the fractal dimension of a Cantor set is $\frac{\ln 2}{\ln 3}$ for $G=3$ and $\frac{\ln 3}{\ln 5}$ for $G=5$. Both for calculations and for measurements, layer thicknesses were chosen to form a *quarter-wave stack*, i.e. if we have dielectrics with refractive index equal to n_1 and n_2 , then the thicknesses are $d_1 = \frac{\lambda_0}{4n_1}$ and $d_2 = \frac{\lambda_0}{4n_2}$, respectively, and the total thickness of the stack will be $D = 2^N d_1 + (3^N - 2^N) d_2$.

3 Theoretical calculations

For theoretical calculations we used a fast simple method based on wave interference and phase-matching boundary conditions. Simple recurrent relations allow us to calculate the transmission coefficient together with the field intensity profile within the structure in a single straightforward procedure, without use of heavy iterative procedures and time-consuming matrix calculations. As an additional 'technical' advantage, the method is applicable to any kind of a layered structure without loss of productivity, unlike transfer-matrix approach and operator notation.

Fig. 2 depicts the calculated transmission spectra of $G=3$ Cantor stacks for the first three generations ($N=1, 2, 3$). We can observe the following features. Firstly, we can see that the number of transmission resonances (peaks) increases as G^N and equals to the total number of layers. Secondly, we see that the spectra exhibit *apparent scalability*, i.e. a transmission spectrum for a given N value contains spectra of all previous generations in 'compressed' state. The compression factor is equal to G . It points to a strong connection between geometrical and spectral properties of a Cantor multilayer structure. Thirdly, we can see that as N increases, not only new peaks appear, but also existing ones tend to split into doublets; that property can be explained in terms of optically connected resonators.. This is also a general property, and the number of peaks in the resulting multiplet in fact equals to $\frac{G+1}{2}$, which yields 2 for $G=3$ and 3 for $G=5$.

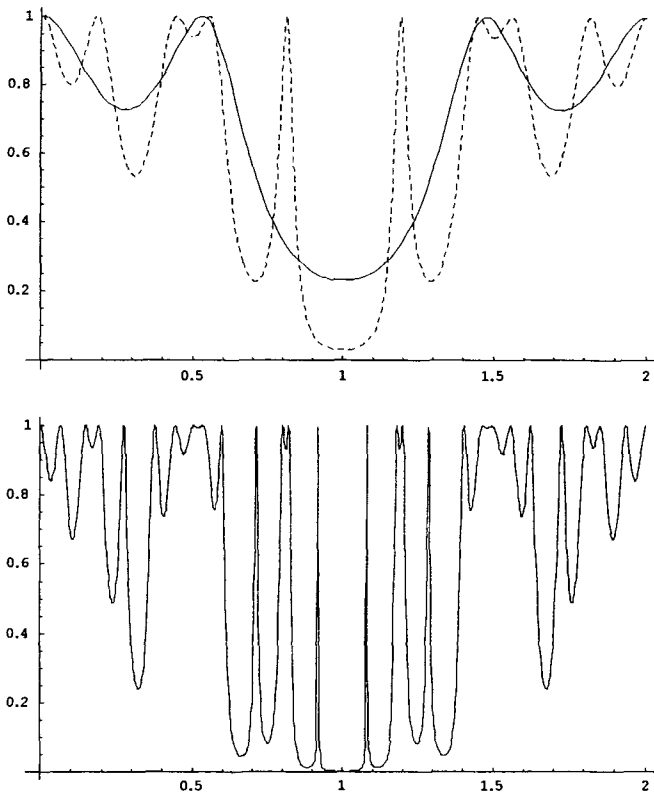


Figure 2. Transmission spectra (transmission coefficient versus normalized frequency) for $G=3$. Cantor multilayers for $N=1, 2, 3$ (respectively *top, solid line; top, dashed line and bottom*) at normal incidence.

4 Experiment

We fabricated a lattice consisting of Na_3AlF_6 ($n_1 = 1.34$) and ZnS ($n_2 = 2.3$) layers by standard optical technology using layer by layer vacuum deposition on a glass substrate. Optical thickness of every layer is equal to $600 \text{ nm}/4$, i.e. $4n_1d_1 = 4n_2d_2 = 600 \text{ nm}$, where d_1, d_2 is the geometrical thickness of layers.

Transmission spectrum was measured using 'Cary 500' spectrophotometer. A good agreement with theoretically predicted spectrum is obtained (Fig. 3). Formation of pronounced resonance transmission peaks is clearly seen. Deviation of experimental

spectrum from the calculated one at the ages of the spectral interval examined is due to the influence of the substrate and dispersion of refraction indexes of the materials used.

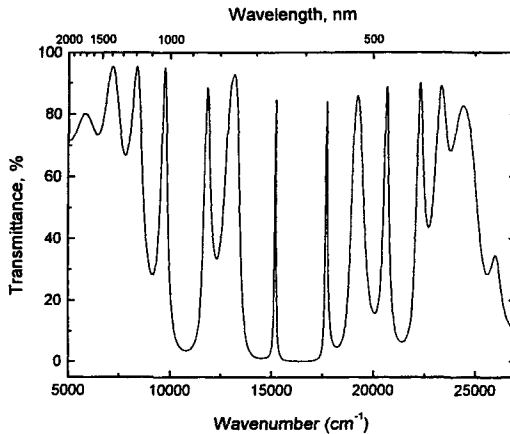


Figure 3. Transmission spectrum for G=3 Cantor multilayers for N=3 at normal incidence (experiment).

5 Conclusion

We demonstrated theoretically and experimentally that fractal multilayered structures possess scalable optical properties. This finding poses a problem of relationship between symmetry of non-periodic lattice and its spectral characteristics. The problem is of general interest with respect to classical waves (electromagnetic, acoustic and others) as well as with respect to electrons in multiple quantum well structures. Taking into account isomorphism of the Schrödinger and Helmholtz equations, the result obtained for optical properties can be replicated to electronic properties. This opens a room for research related to quantum nanoengineering.

Helpful discussions with D. N. Chigrin are acknowledged.

References

1. Chigrin D. N., Lavrinenko A. V., Yarotsky D. A., Gaponenko S. V., *Appl. Phys. A* **68** (1999) 25.
2. Sibilía C., Nefedov I. S., Scalora M., Bertolotti M., *J. Opt. Soc. Amer. B* **15** (1998) 1947.

I-V CURVES OF SHORT INTENTIONALLY DISORDERED SUPERLATTICES IN VERTICAL DIRECTION

A. V. DMITRIEV¹, O. V. PUPYSHEVA¹, P. THOMAS²

¹ *Department of Low Temperature Physics, the Faculty of Physics, Moscow State University
119899 Moscow, Russia*

² *Fachbereich Physik und Zentrum fuer Materialwissenschaften, Philipps-Universitat
Marburg, Renthof 5, D-35032, Germany*

E-mail: Dmitriev@lt.phys.msu.su

Vertical electron transport in semiconductor superlattices with a disorder intentionally introduced into their parameters is studied theoretically. Short superlattices with low carrier concentration and in finite electric field are considered. Electron transmission spectra and current-voltage characteristics are calculated numerically for various types and degrees of the disorder. Virtual scattering by a quasi-localized level with a negative energy is observed for the first time.

1 Introduction

Continuous progress in the superlattice fabrication technology has led to an idea to introduce intentionally a disorder into superlattice parameters, such as nominal values of widths and alloy compositions of the layers.

These superlattices demonstrate a number of novel and interesting physical properties. For example, the luminescence intensity in a disordered system is by several orders of magnitude greater than in a periodic one [1]. An unusual temperature and doping dependence of the vertical conductivity was observed in [2]. The theory of conductivity is, however, weakly developed yet.

In this work, we study theoretically the vertical transport in intentionally disordered superlattices in electric field and calculate their current-voltage characteristics.

2 Theory

We consider the situation when the bias applied to the superlattice is less than the optical phonon energy and hence the most efficient carrier scattering process, LO-phonon interaction, is absent. In this situation we use the tunneling approach to the transport. Only elastic electron scattering by the superlattice potential itself is taken into account. Other scattering processes are ignored. This can be justified in relatively pure and short superlattices with transparent barriers so that the carrier free time is greater than the tunneling time. The temperature should be low enough

to reduce DA-phonon scattering. We assume that the charge carrier concentration is low and neglect electron-electron interaction and screening effects.

We calculate the transmission coefficient T using the effective mass approximation. The superlattice potential is approximated by a sequence of rectangular quantum barriers and wells. Disorder is introduced into their widths and potentials. Other parameters of the layers, e.g. effective electron masses, are assumed to be the same.

The transmission coefficient is calculated using the transfer matrix method (see, for example, [3]). The current-voltage characteristics of the superlattices are derived from the calculated transmission spectra. The tunneling current density along the growth direction (x-axis) equals [4]:

$$J(U) = \frac{em}{2\pi^2\hbar^3} \int_0^\infty T(E_x, U) F(E_x, U) dE_x, \quad F = \int_{E_x}^\infty (f_1(E) - f_2(E, U)) dE,$$

where $T(E_x, U)$ is the transmission coefficient for the particle with the energy $E_x = p_x^2/2m$ at the left border of the superlattice, and under bias U ; $f_1(E)$ and $f_2(E, U)$ are the electron distribution functions at the left and right contacts to the superlattice, respectively.

3 Results and discussion

We considered GaAlAs-, GaAlN- and InAlSb-based superlattices. One of the following four types of disorder was introduced into their parameters: random fluctuations of the widths of the wells or barriers or fluctuations of the potentials of the wells or barriers. The disorder distribution was always uniform and produced by a random number generator. Superlattices with various degrees of the disorder were studied.

The influence of the well parameter fluctuations (diagonal disorder) on the transmission spectrum is much stronger than that of the barrier parameter fluctuations (non-diagonal disorder). For the diagonal disorder a new phenomenon appears, which is absent in a periodic superlattice. Not only the energy levels belonging to different subbands can intersect under bias, but this is true also for the levels from the same subband. The intersection appears when a level which is higher at zero field due to the disorder moves down more rapidly than the other as the field increases due to the different positions of the wells where they are localized. At this voltage the resonant tunneling occurs through two space-separated quasi-localized states within the superlattice, instead of one. This greatly increases the transmission probability at the energy of these states, and hence the current density. As a result, additional peaks appear on $J(U)$ curve in the case of a diagonal disorder.

The energy and field dependence of the transmission coefficient was used for calculations of the current-voltage characteristics depicted in Fig. 1. One can see

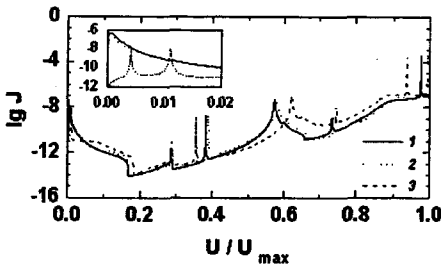


Figure 1. Current-voltage characteristics of the periodic superlattice (curve 1), disordered superlattice with fluctuating barrier widths (curve 2), and disordered superlattice with fluctuating well widths (curve 3).

that there is no prominent difference between the current-voltage characteristics of the periodic superlattice (curve 1) and of one with the off-diagonal disorder (curve 2). However, the fluctuations of the quantum well widths lead to a noticeable shift of the current density maxima and to the drops observed on the characteristics (curve 3). This difference is most evident at low voltages, where the additional maxima are observed, as it is shown in the insert of Fig. 1. These maxima are situated at low voltage because the mean disorder-induced energy level fluctuation in our calculations is small as compared to the inter-subband gaps, that is, the energy of size quantization. As the degree of disorder is increased, the current peaks would shift to higher voltages, approaching the area typical for the peaks in the periodic superlattice.

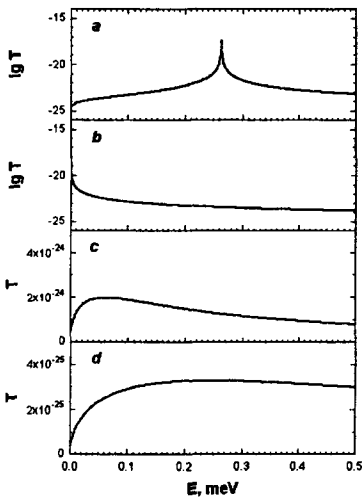


Figure 2. Low-energy part of electron transmission spectra of the periodic superlattice for increasing voltage values. Please note different scales.

As the voltage increases, the energy levels move down one after another and gradually enter the energy interval most populated by the electrons (see Fig. 2(a)). Their movement within this interval corresponds to the regions of slow current growth between the peaks on the current-voltage characteristics. At a voltage when the energy of the level becomes equal to zero (Fig. 2(b)), a sharp current drop takes place because resonant tunneling through this level is no longer possible.

It is interesting that as the voltage is further increased so that the level passes to negative energy values, a small and wide transmission maximum is observed (Fig. 2(c)). Its energy increases and the height decreases as the level moves deeper to negative energy values (below the conductivity band bottom in the left contact), as shown in Fig. 2(c),(d). The maximum is connected with the transition through the level with a small negative

energy. This is a manifestation of the so-called virtual scattering, well known for shallow localized energy levels [5]. At the best of our knowledge, this is its first theoretical observation for scattering by a quasi-localized level (although the level has passed below the bottom of the conductivity band in the left contact, it is still above the bottom of the band in the right contact and hence remains quasi-localized). This latter phenomenon can appear only at a finite voltage applied to a one-dimensional or quasi-one-dimensional system.

References

1. Yamamoto T., Kasu M., Noda S., et al., *J.Appl.Phys.* **68** (1990) 5318.
2. Richter G., Stolz W., Koch S., et al., *Superlatt. and Microstruct.* **74** (1997) 475.
3. Cota E., Jose J. V., Azbel M. Ya., *Phys.Rev. B* **32** (1985) 6157.
4. *Tunneling Phenomena in Solids*, ed. by Burstein E., Lundquist S. (Plenum, New York, 1969).
5. Landau L. D., Lifshits E. M., *Quantum Mechanics: Non-Relativistic Theory* (Pergamon, Oxford, 1977).

PHONON-PLASMON INTERACTION IN TUNNELING GaAs/AlAs SUPERLATTICES: EXPERIMENT AND CALCULATIONS

M. D. EFREMOV, V. A. VOLODIN, V. A. SACHKOV, V. V. PREOBRAZHENSKII,
B. R. SEMYAGIN

*Institute of Semiconductor Physics SB RAS
pr. ak. Lavrent'eva 13, 630090 Novosibirsk, Russia*

E. A. GALAKTIONOV

*Novosibirsk State University
Pirogova Street 2, 630090 Novosibirsk, Russia*

E-mail: efremov@isp.nsc.ru

Phonon-plasmon interaction in tunnelling thin GaAs_n/AlAs_m superlattices (SLs) was studied using Raman spectroscopy. It was observed that when GaAs layers was thinned from 6 to 0.6 monolayers the coupled phonon-plasmon modes became 3D-like, and the interaction of plasmons with LO-phonons of AlAs type takes place. The phonon-plasmon interaction in the case of SLs was numerically modelled on the basis of a microscopic approach. The qualitative agreement of the experiment and the calculations occurs.

1 Introduction

Study of charge carriers tunnelling and phonon-plasmon interaction in A^{III}-B^V superlattices (SLs) is an important problem because in modern micro- and optoelectronics such structures with tunnelling thin barriers are widely used. The properties of quasiparticles in the SLs depend on the thickness of both wells and barriers. Its dispersion could be 2D- or 3D-like as a result of localization or tunnelling.

2 Experimental

The studied SLs were grown by MBE (001) GaAs substrates under condition of (2x4) reconstruction. The set of Si doped and undoped GaAs_n/AlAs_m SLs ($n=6, 3.6, 2.4, 1.2$ and 0.6 ; $m=5$ monolayers in (001) direction) were grown, hereafter these SLs are referred to as 1-5 samples. Concentration of electrons in doped SLs was $2.0 \times 10^{18} \text{ cm}^{-3}$. At this concentration the plasmon frequency in GaAs is close to the frequency of optical phonons [1]. All Raman spectra were registered in quasi-backscattering geometry at room temperature using 514.5 nm line of Ar laser.

3 Results and discussion

The Raman spectra of doped and undoped SLs are shown in Fig. 1. First, consider the AlAs region of the spectra (left). As one can see, for relatively thick SLs (sample 1, 6 MLs GaAs), the width of peaks for doped and undoped SL are nearly equal. In the case of doped sample the peak position shifted to higher energy. The shift may be caused by intersubband optical plasmons interaction with optical phonons, meanwhile intrasubband contribution is negligible due to localization of electrons. Some changes in spectra of doped and undoped SL 2 take place but in the case of SLs 3-5 these changes are dramatic. The coupled modes (for doped SLs marked as LP2) are shifted and broadened. Peaks resulting of scattering on TO modes in these samples are also slightly broadened.

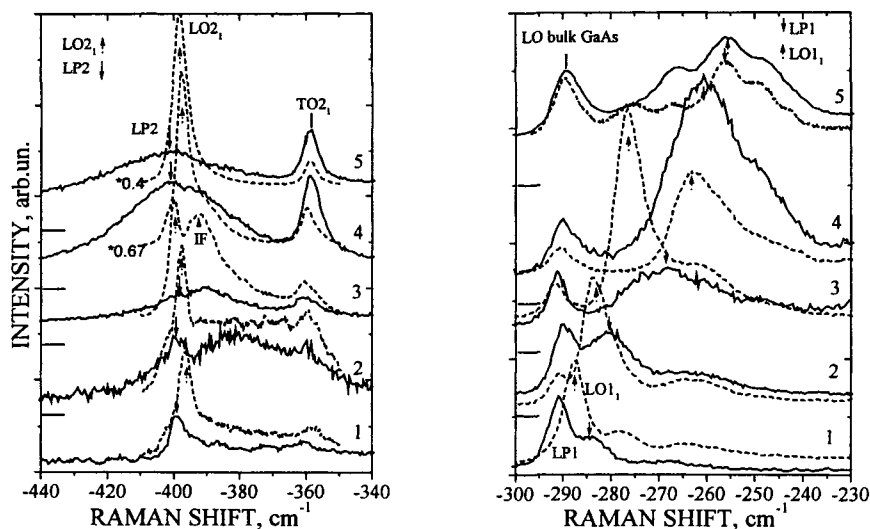


Figure 1. Raman spectra in $Z(YX)\bar{Z}$ geometry for doped (solid lines) and undoped (dashed lines) SLs.

In Raman spectra of undoped SLs 3 and 4 the additional peaks between longitudinal optical (LO) and transverse optical (TO) modes are present. These peaks could be due to scattering on interface (IF) modes. Even though the peaks in the case of doped SLs are very broad, one can also resolve in the Raman spectra of SLs 2-4 two peaks. The additional peaks can be a result of coupling plasmons with the IF modes. The coupling modes in the case of very thin SLs are similar to coupling modes in 3D-case of doped $\text{Ga}_x\text{Al}_{(1-x)}\text{As}$ solid solutions [2]. According to simple consideration using the Kronig-Penny model in the case of SL 4 and 5 the electrons are practically delocalized which is in good agreement with experimental data.

Now, we consider the GaAs region (right). The peak at 291 cm^{-1} in all spectra is due to scattering on bulk GaAs modes of the capping layer and the buffer layer. In the case of doped SLs the capping layer was thicker than in the case of undoped SLs, so for this sample GaAs-bulk peak is more intensive. As one can see, the coupled modes of plasmons with optical phonons of GaAs type (marked as LP1) are shifted in low energy region comparing with pure phonon modes in undoped SLs. The coupled modes are also broader. The position and width of all peaks are presented in Fig. 2. The effect of "softening" modes in the case of doping cannot be explained in frames of macroscopic approach [3]. The zeroes of dielectric constant with phonon and plasmon deposition give the frequencies of these models always bellow the frequencies of pure LO modes. Therefore, the more accurate approach is needed to calculate the dispersion of the coupled phonon-plasmon modes in tunnelling SLs.

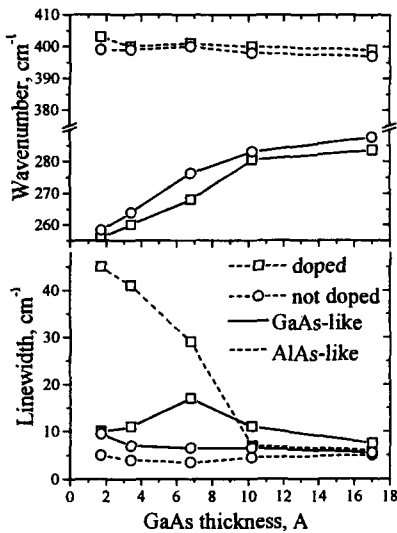


Figure 2. Position and width of coupled phonon-plasmon and LO modes.

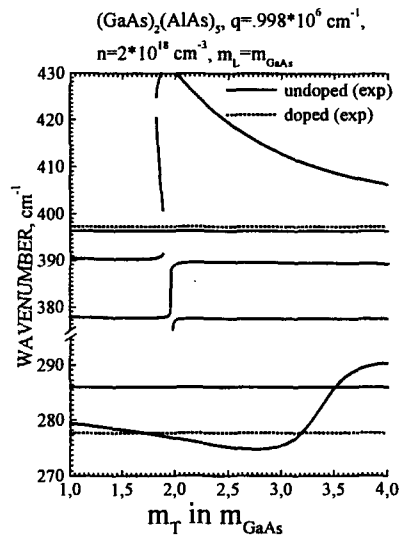


Figure 3. Calculated position of phonon-plasmons in $\text{GaAs}_x/\text{AlAs}_5$ SL.

We use the microscopical approach for calculations of phonon-plasmon mode dispersion. The dynamic matrix of atomic vibrations was taken in "bond-charge" model. Phonons were considered as subsystem in dielectric media with the permittivity defined by electron gas in Lindhard-Mermin approximation [1]. Long range dynamical screening of phonons by electron gas was taken into account by self-consistent solution for the dynamic matrix. The resultant dependence of frequencies of coupled phonon-plasmons on wave vector and frequency was derived as well as corresponding Raman spectra. Some results of calculations are presented in Fig. 3. The mass of electron along GaAs layer (m_e) was the volume mass of electron, and

the mass along direction of SL growth (m_T) was changed. As one can see, at some volumes of m_T , the frequency of phonon-GaAs-type phonon mode is low energy shifted, but the frequency of phonon-AlAs-type phonon mode is high energy shifted. We can observe the similar picture in the experiment. The wavenumbers of LO1 modes of undoped and LP1 and LP2 modes of doped SL 3 are shown for comparison.

In conclusion, experimental and the theoretical results concerning phonon-plasmon interaction in GaAs/AlAs SLs with ultra-thin GaAs layers and tunnelling AlAs barriers were obtained for the first time. The qualitative agreement between the experiment and the calculations is achieved.

4 Acknowledgements

The work has been supported by Russian Foundation for The Basic Research, Grant № 99-02-16668. VAV is grateful to Scientific Council of ISP SB RAS for stipend for young scientists.

References

1. Cardona M., *Light Scattering in Solids IV* (Springer-Verlag, Berlin, 1982).
2. Mintairov A. M., Smekalin K. E., Ustinov V. M., Hvosticov V. P., *Semiconductors* **26** (1992) 614.
3. Volodin V. A., Efremov M. D., Preobrazhenskii V. V., et al., *JETP Lett.* **71** (2000) 698.

NEGATIVE AND PERSISTENT POSITIVE PHOTOCONDUCTIVITY IN P-TYPE $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$

E. V. BOGDANOV, A. A. ILIEVSKY, N. YA. MININA, A. M. SAVIN

Moscow State University

119899 Moscow, Russia

E-mail: bev@mig.phys.msu.su

O. P. HANSEN, C. B. SORENSEN

Niels Bohr Institute

DK-2100 Copenhagen, Denmark

E-mail: oleper@mail.fys.ku.dk

W. KRAAK

Humboldt University

D-10155 Berlin, Germany

E-mail: kraak@physik.hu-berlin.de

Illumination of a double $\text{p-Al}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ heterostructure by a red light emitting diode results in a negative photoconductivity that, after the diode is switched off, slowly relaxes to a positive persistent photoconductivity, characterized by about 1.5 increase of a two-dimensional hole concentration. This metastable state may be explained in a framework of the model in which deep electron traps are supposed to be located above the Fermi level on the inverted heterointerface.

1 Introduction

It was observed previously that the illumination of a single p-type $\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ heterostructure by a red light emitting diode (LED) at liquid helium temperature results in a negative photoconductivity (NPC) that, after the light is switched off, slowly relaxes to the initial resistance in dark [1]. In the present work we report on the effect of a positive persistent photoconductivity detected after illumination by a red LED at liquid helium temperatures in a p-type double heterostructure $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$, that differs from the structure in [1] by the presence of the inverted heterointerface.

2 Methods and results

The double p-type $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ heterostructure was grown by molecular beam epitaxy (MBE) in [001] direction and modulation doped with Be in $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$. The active layers with $2 \times 10^{18} \text{ Be/cm}^3$ were separated from GaAs quantum well by spacers of the widths 500 Å and 250 Å, if there are taken respectively in the growth direction. Samples were cracked from the wafers along <110> directions, which give natural cleavage, and mesa was prepared by photolithography in a Hall bar configuration with current being along [110]. At 1.5 K the hole density in dark is $N = 2.8 \times 10^{15} \text{ m}^{-2}$ and hole mobility $7.0 \text{ m}^2/(\text{V s})$.

Illumination of the samples with the red LED (photon energy 1.9 eV) also caused the NPC effect similar to the one observed in [1]. However in this case, when the LED was switched off, the non-exponential transient process led to the positive photoconductivity (PPC) was characterized by higher values of carrier density and mobility in comparison with the initial state in dark. The initial state in dark could be restored by warming the sample up to room temperature and slow cooling it to 1.5 K.

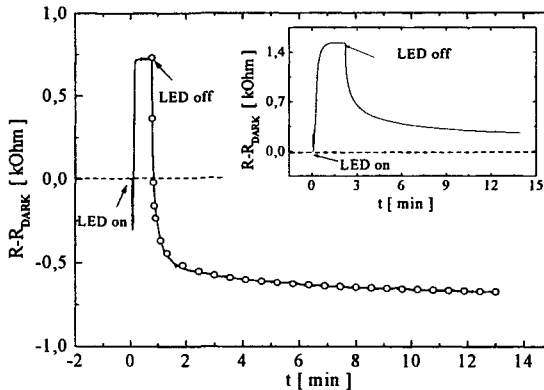


Figure 1. NPC and PPC effects in double p- $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ and single p- $\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ (insert) heterostructures. Open circles are fitting to the logarithmic law.

The carrier concentration was controlled by Hall effect, Shubnikov-de Haas (SdH) oscillations and quantum Hall effect. The numerical values of carrier concentration in dark and the PPC state, calculated from the Hall effects and the frequency of SdH oscillations, are the same within the experimental error about 2 %. In the PPC state we consider the value 1 h after the LED was switched off. For the sake to control our results the single $\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ heterostructure with the normal heterointerface was grown by MBE in the similar conditions and investigated in respect to the red LED illumination. The NPC effect, that relaxed to

the initial stable state in dark after the LED switching off, was detected in agreement with the data from [1] (insert in Fig. 1).

The transient process between NPC and PPC states is not exponential and may be fitted by the logarithmic law (Fig. 1). It should be noted that in [1] the logarithmic law was obtained for recombination of spatial separated charges. But it describes the electron-impurity tunneling at semiconductor heterointerfaces too [2].

3 Discussion

The direct energy gap E_g in $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ is 2.14 eV at 4.2 K and it is larger than the red LED photon energy (1.9 eV). Therefore the direct band to band transitions under illumination are not possible in the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ layer. The electron-hole pair excitation in the GaAs ($E_g=1.43$ eV) layer is possible, but it can not be responsible for the observed effect. Following the conception of the NPC effect developed in [1], we have to suppose the presence of deep donor-like states located a bit below the Fermi level (FL) in the spacer just near the heterointerface. Being below the FL these states are neutral. The band-gap discontinuity in the valence band $\Delta E_v=250$ meV and therefore under illumination electrons may be photogenerated from these states to the conduction band, where they are swept by the junction electric field into the quantum well (QW) and recombine with 2D holes, causing the reduction of their density. As in [1], the decay process to the initial state in dark (Fig. 1) is connected with tunneling of holes from the positively charged excited donor like states back to the QW.

The PPC effect in the double heterostructure is characterized by a considerable increase of the 2D hole concentration compared with one in dark. Since the $\text{p-Al}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ structure differs from $\text{p-GaAs}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ by the presence of the second inverted heterointerface, the excess of 2D holes may be explained if we assume that during illumination some amount of electrons is captured by deep electron traps located on this interface above the FL. The proposed model is illustrated in Fig. 2.

Recent study of the inverted heterointerface in $\text{n-GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{n-AlAs}/\text{GaAs}$ [3,4] reports on the presence of the series of four levels, that originate from intrinsic point defects associated with arsenic vacancies and antisites. In particular, two charge states of the isolated arsenic vacancy V_{As} were identified in $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$. The defects are continuously present near the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ surface during the growth process without being incorporated into the layer. They are regarded to be electron traps with a small barriers for electron capture (below 50 meV for V_{As}) and thermal activation energies in the range of 0.28-0.93 eV for $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$. The concentration of electron traps depends on the growth mode and may vary from $1 \times 10^{12} \text{ cm}^{-2}$ to $1 \times 10^{10} \text{ cm}^{-2}$ [4].

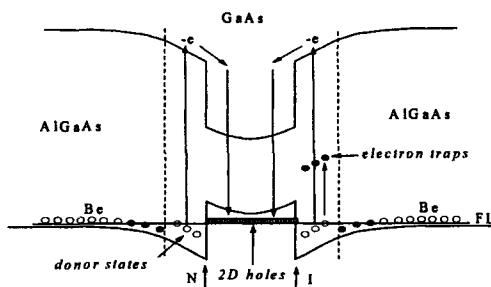


Figure 2. Sketch for illumination in the proposal PPC model.

As far as the origin of the mentioned above intrinsic defects is determined by the specific nature of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ growth process, but not by impurities, the same defects should arise also at p-type inverted heterointerfaces. It means that electron traps at the inverted heterointerface in $\text{p-Al}_{0.5}\text{Ga}_{0.5}\text{As/GaAs/Al}_{0.5}\text{Ga}_{0.5}\text{As}$, supposed to be responsible for the observed PPC effect, are most possible identified as intrinsic point defects [3,4]. The increase of hole mobility in the PPC state may be explained by an increase of screening effect with growing hole concentration as well as by a decrease of interfacial charge states because of the electron capture process.

4 Acknowledgements

The work was supported by RFBR under Project № 00-15-96784.

References

1. Chou M. J., Tsui D. C., Weinmann G., Negative photoconductivity of two dimensional holes in $\text{Al}_x\text{Ga}_{1-x}\text{As/GaAs}$ heterojunction, *Appl. Phys. Lett.* **47** (1985) pp. 609-611.
2. Schubert E. F., Fisher A., Ploog K., Electron-impurity tunneling in selectively doped n-type $\text{Al}_x\text{Ga}_{1-x}\text{As/GaAs}$ heterojunction, *Phys. Rev. B* **31** (1985) pp. 7937-7946.
3. Krispin P., Hey R., Kostial H., Intrinsic origin and composition dependence of deep-level defects at the inverted $\text{GaAs/Al}_x\text{Ga}_{1-x}\text{As}$ interface grown by molecular-beam epitaxy, *J. Appl. Phys.* **77** (1995) pp. 5773-5781.
4. Krispin P., Hey R., Kostial H., Ploog K. H., Growth mode-related generation of electron traps at the inverted AlAs/GaAs interface, *J. Appl. Phys.* **83** (1998) pp. 1496-1498.

RAMAN AND PHOTOLUMINESCENCE STUDIES OF THE INTERFACE RECONSTRUCTIONS IN GaAs/AlAs SUPERLATTICES GROWN ON (311) AND (001) SURFACES

M. D. EFREMOV, V. A. VOLODIN, V. A. SACHKOV, V. V. PREOBRAZHENSKII,
B. R. SEMYAGIN

*Institute of Semiconductor Physics SB RAS
pr. ak. Lavrent'eva 13, 630090 Novosibirsk, Russia*

E. A. GALAKTIONOV, A. V. KRETININ

*Novosibirsk State University
Pirogova Street 2, 630090 Novosibirsk, Russia*

E-mail: efremov@isp.nsc.ru

The GaAs/AlAs superlattices (SLs) grown on facet surfaces (311)A,B and (100) surface were studied using Raman and photoluminescence (PL) spectroscopy. Sharp differences in Raman and PL spectra of the ultrathin SLs grown on (311)A and (311)B surfaces were observed. These effects probably are result of differences in interface reconstructions. The observed phonon anisotropy of (311)A SLs can be indirect evidence of anisotropic structure of surface quantum objects formed on (311)A GaAs. The PL peaks of (311)A and (311)B SLs differ both the intensities and the positions. In the Raman spectra of the SL containing GaAs submonolayers grown on (2x4) reconstructed (100) surface, the triplet Raman peak corresponding to scattering on GaAs-like confined LO phonons was observed. The triplet structure appears due to additional lateral confinement of LO phonons in GaAs quantum islands. Calculations of Raman spectra were carried out using the models of rigid ions, bond charge and Wolkenstein bond polarisability. The theoretical Raman spectra of the islands grown (in the context of a known model) on the (001)-(2x4) reconstructed surface are in surprisingly good agreement with the experimental ones. The calculations show that 70 % of the islands contains less than 18 Ga atoms, what is in very good agreement with the known STM data.

1 Introduction

The III-V heterostructures are widely used in optoelectronics and telecommunications. The properties of devices based on such heterostructures depend on the interface structure. For atomic scale studies of the interface, the destructive and expensive techniques, such as STM and HREM are usually used. Raman spectroscopy is non-destructive and giving express information method to study the heterostructures [1]. Confinement of optical phonons and dependence of its frequencies on size and structure of quantum objects are appropriate tools for testing of structure of the quantum objects and the interfaces.

2 Experimental

The studied SLs were grown by MBE on (001), (311)A and B GaAs substrates. In some growth conditions, the GaAs (311)A surface is anisotropic [2,3], and in process of heteroepitaxy, the lateral SLs (LSLs) containing periodic corrugated GaAs and AlAs layers can be formed [2]. The period of corrugation is 3.2 nm in $\langle 01\bar{1} \rangle$ direction. The set of GaAs_n/AlAs_m SLs were grown with parameters shown in the Table. All the Raman spectra were registered in quasi-backscattering geometry at room temperature using 488 nm line of Ar laser.

Table. Specification of the GaAs_n/AlAs_m SLs.

Substrate orientation			Thickness		Periods,
(001)	(311)A	(311)B	GaAs, Å	AlAs, Å	numbers
S1	A1	B1	20.4	20.4	100
S2	A2	B2	17.0	13.6	100
S3	A3	-	10.2	13.6	100
S4	A4	B4	8.5	20.4	200
S5	A5	B5	6.8	13.6	200
S6	A6	B6	3.4	13.6	300
S7	A7	B7	1.7	13.6	400

3 Results and discussion

3.1 Localized TO phonons in (311)A and (311)B SLs

The Raman spectra of LSLs and SLs grown on (311)A and B surfaces are shown in Fig. 1. Due to symmetry selection rules, the TO_y and TO_x modes (atoms vibrate

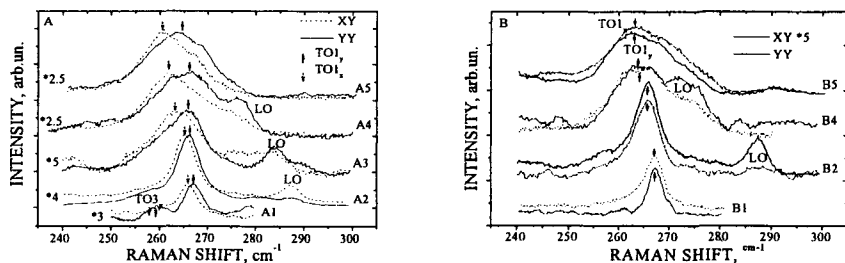


Figure 1. Raman spectra in $Z(YY)\bar{Z}$ geometry (solid) and $Z(YX)\bar{Z}$ geometry (dashed line) for the SLs grown on the surfaces: a) (311)A; b) (311)B.

along the crystallographic directions Y and X, along and transverse to GaAs quantum wires) are observed in polarisation geometries $Z(YY)\bar{Z}$ and

$Z(YX)\bar{Z}$ respectively. In Fig. 1(a), one can see splitting of confined TO modes of the first order TO_{1y} and TO_{1x} . The splitting increases with decreasing of average thickness of GaAs layers. The SLs on GaAs (311)B surfaces were grown in the same conditions and have the same thickness of layers as in the case of the (311)A surfaces to make sure that the effect of splitting is caused just by the GaAs (311)A surface corrugation. The Raman spectra of (311)B samples are presented in Fig. 1(b). It is seen, that in this case the effect of splitting of TO modes is negligible. In the case of LSLs the splitting sharply increases when the average thickness of GaAs layers is equal or less than the height of facets in one of the model of (311)A surface reconstruction (6 monolayers) [2]. This fact can be an indirect evidence of the quantum wire-like growth model [2].

3.2 PL spectra of (311) A and B SLs

Results of the photoluminescence (PL) study also confirm the strong difference in structures of (311)A LSLs and (311)B SLs. The PL spectra of samples A2, B2, and S2 (see Table) are shown in Fig. 2. Maximum of PL for (311)A LSL is shifted to short-wavelength region and its intensity is 50 times higher than that for (311)B and (001) SLs. The PL spectra of (311)B and (001) SLs are very similar. It is believed that difference between PL spectra of SL grown on (311)B surface and LSL grown on (311)A surface is a result of (311)A surface corrugation.

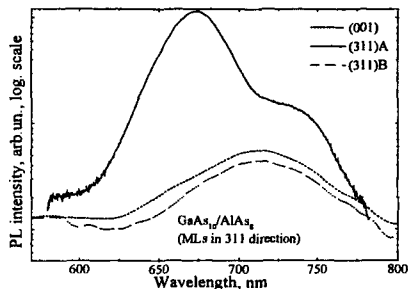


Figure 2. PL spectra of SLs and LSL.

3.3 Study of GaAs quantum islands

To reveal the shapes of the GaAs islands formed on (001)-(2x4) reconstructed AlAs surface under condition of GaAs submonolayer covering, the comparing analysis of experimental and calculated Raman spectra was carried out. The shapes of islands were chosen on a basis of a known model of the island nucleation on (2x4) reconstructed (001) surface [5]. The calculations had been made using Born approximation, model of rigid ions, bond-charge model and bond polarisability model of Wolkenstein [1].

The experimental and calculated Raman spectra are shown in Fig. 3. The average GaAs cover for the experimental structure was 0.6 monolayer. In the beginning of the Ga deposition on (001)-(2x4) reconstructed surface the Ga adatoms can coat As dimer rows along $[1\bar{1}0]$ direction [5]. The calculations were carried out with account of scattering from GaAs islands of 10 various shapes. The contribution of the islands with a specific shape in the total calculated Raman spectrum was

determined in the approximation of the theoretical spectrum to the experimental one using the method of least squares. As one can see in Fig. 3, the calculated spectrum

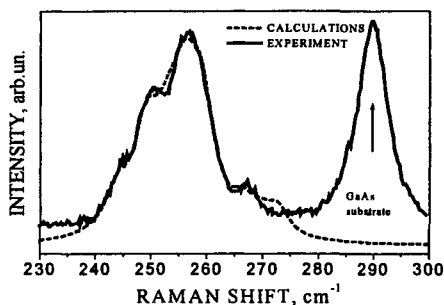


Figure 3. Experimental and calculated Raman spectra of $\text{GaAs}_{0.6}/\text{AlAs}_{0.4}$ SL.

is in remarkable agreement with the experimental ones. That is very surprising, but the average GaAs cover calculated from the contribution of the islands of all shapes is occurs to be equal to the experimental one (0.6 monolayer) with the very good accuracy. According to the result of the approximation, about 70 % of GaAs islands contain less than 18 Ga atoms [6]. This result is in good correlation with the STM data [5] that the small islands are more stable.

4 Acknowledgements

This work was supported by Russian Fund of Basic Research, Grants № 99-02-16668. VAV is grateful to Scientific Council of ISP SB RAS for stipend for young scientists.

References

1. Cardona M., Günterodt G., *Light Scattering in Solids V. Superlattices and Other Microstructures* (Springer-Verlag, Berlin, 1989).
2. Nötzel R., Ledentsov N. N., Däwerits L., et al., *Phys. Rev. B* **45** (1992) 3507.
3. Geelhaar L., Marquez J., Jacobi K., *Phys. Rev. B* **60** (1999) 15890.
4. Volodin V. A., Efremov M. D., Preobrazhenskii V. V., et al., *JETP Lett.* **66** (1997) 47.
5. Itoh, Bell G. R., Avery A. R., et al., *Phys. Rev. Lett.* **81** (1998) 633.
6. Efremov M. D., Volodin V. A., Preobrazhenskii V. V., et al., *JETP Lett.* **70** (1999) 75.

INVESTIGATION OF SURFACE MORPHOLOGY FEATURES AND LOCAL PHOTOELECTRIC PROPERTIES OF InAs/GaAs QUANTUM DOT STRUCTURES

V. YA. ALESHKIN, A. V. BIRYUKOV, N. V. VOSTOKOV,
S. V. GAPONOV, V. M. DANIL'TSEV, V. L. MIRONOV, A. V. MUREL,
O. I. KHRYKIN, V. I. SHASHKIN

*Institute for Physics of Microstructures of RAS
603600 Nizhny Novgorod, Russia*

E-mail: mironov@ipm.sci-nnov.ru

The scanning probe microscopy methods have been applied to investigate morphology and local photocurrent spectra in InAs/GaAs structures with quantum dots grown near a sample surface. The influence of a strong electric field on the STM spectrum was investigated.

1 Introduction

Probe microscopy methods are currently in wide use for study of quantum-size structure properties. The trend in these investigations is observation of local luminescence in such structures with the methods of near-field optical microscopy [1-3] and electroluminescence excited in the STM tunnel contact (the so-called STM-cathodoluminescence) [4-6]. Recently, the photo-assisted STM technique [7,8] was used in our group for investigation of local photocurrent in quantum-size heterostructures [9,10]. In this paper we report the results of STM studies of the effect produced by an electric field on the local photocurrent spectra in InAs/GaAs structures with quantum dots grown near the sample surface.

2 Experiment

GaAs/InAs/GaAs quantum dot heterostructures were grown by the metalorganic vapor-phase epitaxy method in vapor-gaseous medium $\text{H}_2\text{-Ga}(\text{CH}_3)_3\text{-AsH}_3\text{-In}(\text{CH}_3)_3$ at atmospheric and at low pressures. The growth temperature was varied in the range of 480-600 °C. As substrates we used doped GaAs wafers 2°-misaligned relative to the (100) plane in the [111] direction. First, the substrates were coated with a 0.2 μm thick buffer layer of GaAs at 600 °C. Then, at 480 °C we formed a layer of InAs quantum dots. At the final stage of this process the InAs islands were overcoated with a GaAs layer at a rate of about 20 nm/min at 480 °C. The epitaxial structures featured n-type conductivity and the carrier concentration was $\sim 2 \times 10^{16} \text{ cm}^{-3}$.

The surface morphology of the sample was studied with a "Solver P4" atomic-force microscope (NT MDT, Zelenograd, Russia). Investigation of the local

photoelectric properties was supported by the tunneling microscope (STM) connected with the optical system facility [11] developed at the IPM RAS. The experiments were conducted in the open air. To avoid oxidation of the quantum dots layer during the current measurement procedure we used a vacuum oil conservation of surface. Sample area under the STM probe was optically pumped through the GaAs substrate with a halogen lamp radiation transmitted through monochromator. Photocurrent was measured as a difference between the current in the backward branch of the current-voltage characteristic by illumination of the probe-sample contact, and the dark current.

3 Results and discussion

As shown by our AFM studies, the early stages of the InAs islands overgrowth with GaAs have some specific features. Fig. 1(a, b) demonstrates the surface morphology of two samples differing in the thickness of the GaAs covering layer.

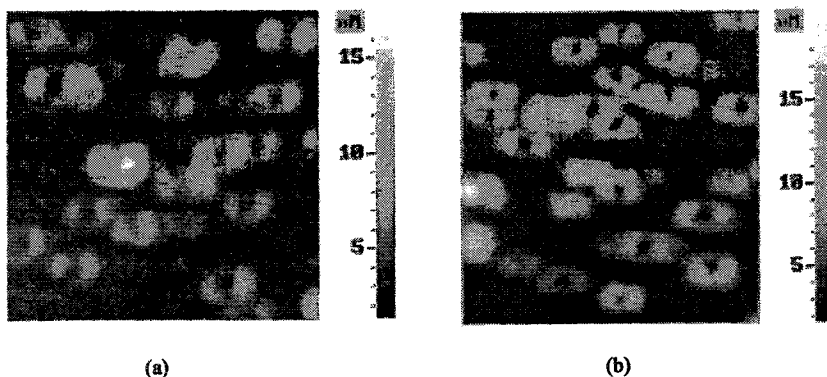


Figure 1. AFM images of InAs/GaAs structure with quantum dots grown near the surface: (a) 1.5 nm GaAs covering layer (image size is 550x550 nm); (b) 2 nm GaAs covering layer (image size is 600x600 nm).

The characteristic lateral dimensions of quantum dots prior to covering were ~ 50 nm and the average height was ~ 10 nm. Deposition of a 2 nm thick covering layer was seen to cause a preferred growth of GaAs near the islands, so the overgrown islands were rounded with a dip on the top, and their lateral dimensions came to about 100 nm. Such a shape of the islands is apparently associated with the processes of surface diffusion since islands are sinks for the atoms adsorbed at the surface. As the covering layer thickness was growing to more than 4 nm, we saw the dips on the island tops disappear and the surface relief smooth out.

The spectral dependences of a local STM photocurrent in such structures feature a series of peaks corresponding to the carrier transition between different states of the energy spectrum from a quantum-size structure (Fig. 2(a)). The short-wave peak with the energy of ~ 1.397 eV seems to be determined by carbon in the

GaAs epitaxial layer, which has the acceptor level at 26 meV above the valence band of GaAs. According to the calculations, the interband transition energy in the InAs wetting layer at room temperature is 1.377 eV, which is in good agreement with the value for the second peak in the photocurrent spectra. The long-wave peaks apparently correspond to transitions from the excited hole states in QDs to the electron levels in the wetting layer and the excited electron states in QDs.

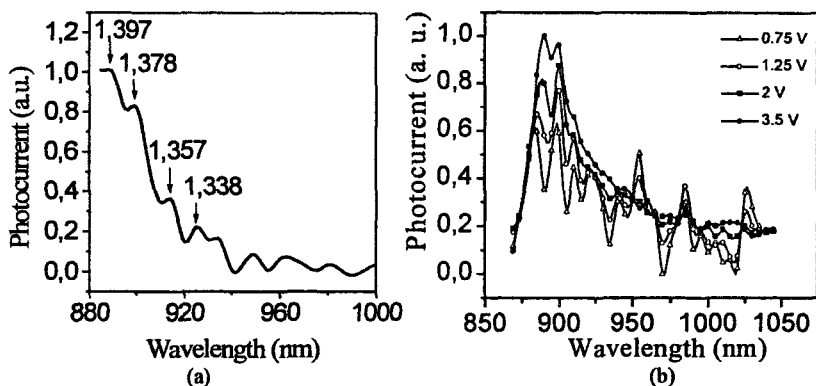


Figure 2. STM spectra of photocurrent in structures with InAs/GaAs quantum dots located near the surface. Thickness of the covering GaAs layer is 2 nm. (a) One spectra. (b) Multiple spectra for different values of the tunneling gap voltage.

We investigated the effect of electric field on position and intensity of the STM photocurrent peaks corresponding to the quantizing levels. The spectral curves of the local photocurrent in QD structures for different values of the tunneling gap bias are shown in Fig. 2(b). We can see a few peculiarities in these spectra. The peaks in the short-wave part ($\lambda \leq 950$ nm) broaden and grow in intensity voltage increases. A different situation is observed in the long-wave part of the spectrum ($\lambda \geq 950$ nm) where the peaks intensity falls off while they broaden with a higher voltage. The increase in the local photocurrent in the short-wave part of the spectrum can be explained by the Franz-Keldysh effect in the bulk GaAs layer adjacent to the tunneling gap where electric fields are high. When light is being absorbed in a high electric field through tunneling of the charge carriers there is an increase in the absorption coefficient in the region of quantum energies less than the band gap width. A similar rise of photocurrent in this spectral region is also observed in structures without quantum objects and it associated with the electric field effect on bulk electron states.

Different effect is produced by the electric field on the intensity of optical transitions between localized states. In a high electric field the mean coordinates of the electron and hole localized states in quantum dots move in opposite directions thus causing the overlap integral of the wave functions for the initial and final states to decrease. This in its turn diminishes the probability of an optical transition

between these states. Besides, an electric field delocalizes the localized states, as there appears a non-zero probability of a tunnel transition to the continuous spectrum states, resulting in shortening and spreading of the corresponding absorption lines.

Spreading of the peaks depends on the time of electron tunneling from the localized states to a continuous spectrum state. It is seen in Fig. 2(b) that the peaks in the spectral region corresponding to the localized-states-assisted transitions become smaller and broader with a higher voltage and practically vanish at 3.5 V. The latter is likely to imply that the frequency of tunnel escape from the excited states involved in the absorption at this voltage becomes comparable with the value of the localization energy divided by the Plank constant, so the states actually becomes delocalized.

4 Conclusion

We studied morphology and local photocurrent in GaAs/InAs/GaAs heterostructures with InAs quantum dots grown near the sample surface. It was found that the electric field affects the characteristics of optical transitions in the STM spectra of the local photocurrent. A higher photoresponse in the short-wave part of the spectrum is believed to be related the Franz-Keldysh effect in bulk electron states, whereas a decrease in the intensity and broadening of the peaks can be explained by the influence of the electric field on the wave function of excited localized states in quantum dots.

The work was supported by the RFBR grants No 98-02-16625, 99-02-16139, 00-02-16486, 00-02-81050.

References

1. Harris T. D., Gershoni D., et al., *Semicond. Sci. Technol.* **11** (1996) 1569.
2. Chavez-Pirson A., Temmo J., et al., *Appl. Phys. Lett.* **72** (1998) 3494.
3. Phalke D., Manke I., et al., *Appl. Surf. Sci.* **123/124** (1998) 400.
4. Markmann M., Zrenner A., *Phys. Stat. Sol. (a)* **164** (1997) 301.
5. Grundmann M., Christen J., et al., *Phys. Rev. Lett.* **74** (1995) 4043.
6. Lindahl J., Pistol M.-E., et al., *Appl. Phys. Lett.* **68** (1996) 60.
7. Akari S., Lux-Steiner M. Ch., et al., *J. Vac. Sci. Tech. B* **9** (1991) 561.
8. Yamamoto H., Kamiya I., et al., *Jpn. J. Appl. Phys.* **38** (1999) 3871.
9. Aleshkin V. Ya., Biryukov A. V., et al., *In Physics, Chemistry and Application of Nanostructures* (World Scientific, Singapore, 1999) 119.
10. Aleshkin V. Ya., Biryukov A. V., et al., *Pis'ma Zh. Tekh. Fiz.* **26** (2000) 3.
11. Volgunov D. G., Gaponov S. V., et al., *Inst. and Exp. Tech.* **41** (1998) 123.

CONTROLLABLE ONE-DIMENSIONAL PHOTONIC STRUCTURES WITH *n-i-p-i* CRYSTAL LAYERS

V. N. GUSYATNIKOV, I. S. NEFEDOV, YU. A. MOROZOV

*Institute of Radioengineering and Electronics, RAS Saratov Department
410019 Saratov, Russia*

E-mail: victor@mail.saratov.ru

V. K. KONONENKO, D. V. USHAKOV

*Stepanov Institute of Physics, NASB
220072 Minsk, Belarus*

E-mail: lavik@dragon.bas-net.by

The availability of *n-i-p-i* crystal layers in periodic structures with a photonic band gap has been considered. It is shown that such photonic structures can be attractive as low-threshold optical switches. The dispersion and transmission characteristics of the structures are examined at high excitation levels where light amplification in the *n-i-p-i* superlattice layers occurs. Properties of optical resonators with the photonic band gap structures in these conditions are discussed.

1 Introduction

In recent years, the interest in multi-layer periodic structures forming a photonic band gap (PBG) has increased because of their attractive application for controllable optical switches and other non-linear optical devices [1,2]. In particular, such periodic GaAs-AlGaAs structures can be used as low-threshold optical gates [2]. The main feature of the gates is the control of the PBG edge by light at the wavelengths near the GaAs absorption edge due to the change of the index of refraction in the active layers under the optical excitation. The wavelength of controlled light corresponds to the PBG edge in the region of 1.5 μm .

In the present work, possibilities to use *n-i-p-i* superlattices as optically controllable active layers in PBG structures are investigated. Described photonic structures with *n-i-p-i* layers are attractive for devices of optical switching and narrow-band tunable light emitting devices.

2 Dispersion characteristics of *n-i-p-i* layers

In general, one-dimensional PBG structures consist of the quarter-wave stack of alternating layers of different dielectric materials. We consider properties of such a photonic structure in the GaAs-AlGaAs system where the absorption layers with

optical controllable parameters are the GaAs *n-i-p-i* crystal layers. In particular, the active *n-i-p-i* layers can be in the form of δ -doped semiconductor superlattices.

In this case, the donor and acceptor concentrations are assumed to be $N_a = N_d = 10^{20} \text{ cm}^{-3}$, width of doped *n*- and *p*-type regions $d_n = d_p = 1 \text{ nm}$, thickness of *i*-layers $d_i = 8 \text{ nm}$. Under optical excitation, current carrier concentration in the *n-i-p-i* layers increases. Therewith, the difference in the quasi-Fermi levels ΔF grows and conditions of radiation absorption and refraction change as well.

Dispersion characteristics of the *n-i-p-i* layers are shown in Fig. 1. Dependencies of the extinction coefficient κ and change in the refraction index Δn at different wavelengths λ on the excitation level ΔF have been calculated according to the Kramers-Kronig relation taking into account the transformation of the potential relief of the doping superlattice under optical or electric excitation. Effects of the density state tails, screening of the impurity electrostatic potential, and shrinkage of the energy band gap are included too [3,4]. The quantised change in the refraction index Δn is related to the filling of the subband levels by current carriers at the excitation of the layers. At definite values of ΔF , the extinction coefficient κ becomes negative, i.e., light amplification occurs in the certain interval of wavelengths. Here, the normalized parameter $\kappa_0(\lambda)$ is the initial extinction coefficient at the thermodynamic equilibrium ($\Delta F = 0$). The index of refraction of the *n-i-p-i* layers is estimated as a sum of Δn and the refraction index for the GaAs host material.

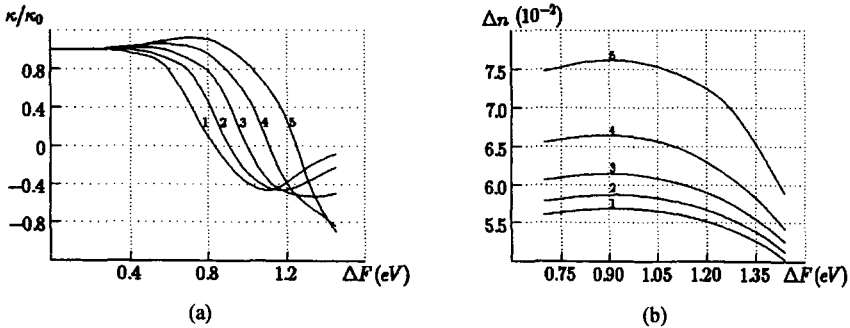


Figure 1. Dependencies (a) of the extinction coefficient κ and (b) quantised refraction index Δn at different wavelengths λ on the excitation level ΔF . (1) $\kappa_0 = 9.50 \times 10^{-6}$, $\lambda = 1500 \text{ nm}$, (2) $\kappa_0 = 3.70 \times 10^{-5}$, $\lambda = 1375 \text{ nm}$, (3) $\kappa_0 = 1.68 \times 10^{-4}$, $\lambda = 1250 \text{ nm}$, (4) $\kappa_0 = 8.71 \times 10^{-4}$, $\lambda = 1125 \text{ nm}$, (5) $\kappa_0 = 4.60 \times 10^{-3}$, $\lambda = 1000 \text{ nm}$.

To find connection between ΔF and the exciting radiation power P in the layers, the following approach is used. It is assumed that the quantum yield at the excitation of the controllable layers in the one-dimensional PBG structure equals to 1, i.e., every absorbed quantum produces one electron-hole pair. Concentrations of non-equilibrium carriers are found from the stationary continuity equation that determines the simple relation between the excitation level ΔF and the generation rate at the absorption of excitation quanta. The rate of the carrier generation per unit

volume in a definite *n-i-p-i* layer is equal to $kP/h\nu_{\text{exc}}$, where k is the absorption coefficient and $h\nu_{\text{exc}}$ is the energy of excitation quanta. The spectrum of absorption $k(\lambda)$ is connected with the spectrum of the extinction coefficient as $k = 4\pi\kappa\lambda$.

The increase of the two-dimensional concentration of electrons n versus the difference in the quasi-Fermi levels ΔF is shown in Fig. 2(a). Using the dependence $n(\Delta F)$, from the relation between $kP/h\nu_{\text{exc}}$ and ΔF , which is given in Fig. 2(b), one can evaluate the effective lifetime of carriers at the radiative recombination. For the *n-i-p-i* structure examined, values of the effective life-time of carriers cover a wide range from 1 ms at a low-intensity excitation to 10 ns at high excitation levels.

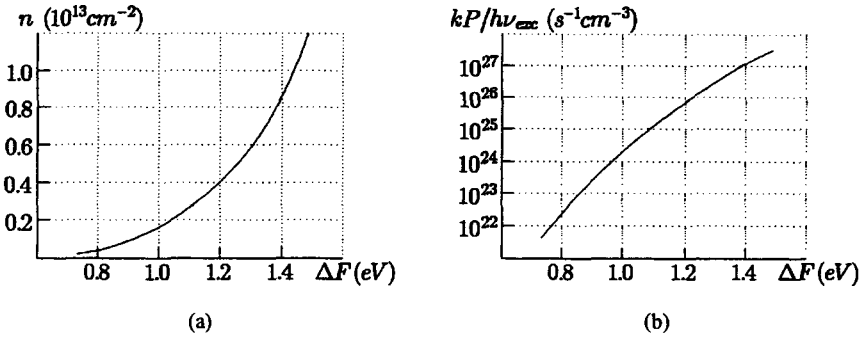


Figure 2. Dependencies (a) of the electron concentration n and (b) rate of excitation $kP/h\nu_{\text{exc}}$ on the quasi-Fermi level difference ΔF in the *n-i-p-i* layers of the photonic structure.

3 Optical switching

The iteration technique of account of the transmission characteristics of PBG structures periodical in one direction is described in detail previously [2]. In Fig. 3, the module of the complex amplitude coefficient of transmission T versus the wavelength λ near the PBG edge is shown for the 40-period $\text{GaAs-Al}_{0.3}\text{Ga}_{0.7}\text{As}$ structure at different values of the input power P_{exc} and excitation wavelength λ_{exc} . The structure contains active *n-i-p-i* layers of the thickness of 0.11 μm , corresponding with the 6-period doping superlattice, and the $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ layers of thickness equal to 0.12 μm . In this case, the PBG centre fits at the initial conditions of $\Delta F = 0$ to the wavelength of 1.45 μm .

As seen, under the excitation of the active *n-i-p-i* layers, the low-energy PBG edge is shifted to the long-wavelength side because of increasing the refraction index in the layers from the filling of the subband levels by current carriers. The quantity of the shift is determined by the distribution of the quasi-Fermi level difference in the layers along the photonic crystal that depends on the wavelength λ_{exc} of controlling light. At the higher levels of excitation of the structure the low-energy PBG edge has to be shifted back.

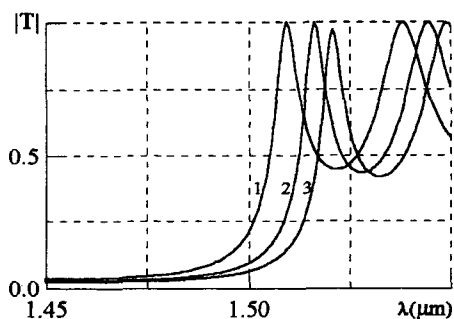


Figure 3. Transmission spectra of the 40-period photonic structure with *n-i-p-i* layers. (1) $P_{\text{exc}} = 0$, (2) $P_{\text{exc}} = 10 \text{ kW/cm}^2$, $\lambda_{\text{exc}} = 0.90 \text{ } \mu\text{m}$, (3) $P_{\text{exc}} = 10 \text{ kW/cm}^2$, $\lambda_{\text{exc}} = 0.98 \text{ } \mu\text{m}$.

In the spectral range 0.8 to 1.1 μm , the transmission coefficient $|T|$ is markedly greater than 1. It results from the appearance of the light amplification at high excitation levels of the *n-i-p-i* layers.

Our calculations show that the resonant amplitude peaks $|T|$ are very sensitive to the spectral displacement of PBG and less sensitive to the excitation light wavelength. The gain of resonators based on PBG crystals with active *n-i-p-i* layers can exceed more than two orders the gain for ordinary Fabry-Perot cavities with the same optical thickness of active medium.

4 Acknowledgements

The present work is supported by the grants RFFR 00-02-81022 and F99R-119.

References

1. Scalora M., Dowling J. P., Bowden C. M., Bloemer M. J., Optical limiting and switching of ultrashort pulses in nonlinear photonic band gap materials, *Phys. Rev. Lett.* **73** (1994) pp. 1368-1371.
2. Nefedov I. S., Gusyatinikov V. N., Optically controlled GaAs-GaAlAs photonic band gap structure, *J. Optics A: Pure and Applied Optics* **2** (2000) pp. 344-347.
3. Ushakov D. V., Kononenko V. K., Variation of the potential relief and emission spectra in doping superlattices under excitation, In *Physics, Chemistry and Application of Nanostructures* (World Scientific, Singapore, 1997) pp. 121-124.
4. Kononenko V. K., Manak I. S., Ushakov D. V., Optoelectronic properties and characteristics of doping superlattices, In *Proc. SPIE* **3580** (1998) pp. 10-27.

INFLUENCE OF ELECTRON IRRADIATION ON CARRIER RECOMBINATION AND INTRADOT RELAXATION IN InGaAs/GaAs QUANTUM DOT STRUCTURES

N. A. SOBOLEV

*Department of Physics, University of Aveiro
3810-193 Aveiro, Portugal*

and

*Institute of Solid State and Semiconductor Physics
220072 Minsk, Belarus*

A. CAVACO, M. C. CARMO

*Department of Physics, University of Aveiro
3810-193 Aveiro, Portugal*

H. BORN, M. GRUNDMANN^{*)}, F. HEINRICHSORFF, R. HEITZ, A. HOFFMANN,
D. BIMBERG

*Institute of Solid State Physics, Technical University of Berlin
10623 Berlin, Germany*

E-mail: sobolev@fis.ua.pt

The influence of high-energy electron irradiation on the time-resolved photoluminescence (PL) of quantum dot (QD) and quantum well (QW) InGaAs/GaAs structures are investigated. Both rise and decay kinetics is changed due to radiation-induced defects. The decay kinetics of as-grown QWs and QDs can be described by a single time constant. The irradiated QWs still exhibit the single exponential decay but with the less time constant, whereas the second faster component appears in the PL decay of QDs along with the component present prior to irradiation. Thus, we observed interaction of confined carriers with radiation-induced defects inside or near the QDs.

1 Introduction

In the past few years, quantum dot structures have attracted increasing interest due to their outstanding performance (for a review see, e.g., [1] and references therein). One of the most important promises of QD nanotechnology is the increased tolerance for defects [2]. Higher quantum efficiency becomes possible with the basic argument that localized carriers will exhibit reduced migration to non-radiative centers. Such property is advantageous for active layers in matrix

^{*)} Present address: Universität Leipzig, Institut für Experimentelle Physik II, Linnéstr. 5, D-04103 Leipzig, Germany

materials with a high number of structural defects. The tolerance to radiation-induced defects is of crucial importance in atomic energy and space applications.

Despite this, only little research has been performed with respect to radiation defects in quantum dots. The radiation resistance against damage due to 50 keV manganese ion implantation [3] and defects created by a 300 eV argon ions [4] was found to be greater for QDs than for QWs. Recently, studies of 1.5 MeV proton and 2 MeV electron irradiation of InGaAs/GaAs QD structures were undertaken, and an enhanced radiation tolerance of QDs as compared to analogous quantum wells (QWs) were reported [5,6]. The effect of irradiation with 8.56 MeV phosphorous ions and 2.4 MeV protons on the properties of QD and QW lasers has been investigated [7,8]. A higher stability of the QD devices was found.

On the other hand, possible tunneling of captured charge carriers off the high-lying states in the dots to neighboring defects in the barrier material has been used to explain the absence of the phonon bottleneck in the carrier intradot relaxation [9]. However, the existence of this mechanism has never been proved experimentally. The most obvious way to check it is to vary the defect concentration in a sample and to investigate resulting changes in the time-resolved photoluminescence (TRPL).

We report the study of the influence of electron irradiation on TRPL of InGaAs/GaAs QD and QW structures. The TRPL measurements reveal a shortening of the rise and decay times in both QWs and QDs, but the behavior of both the types of samples is qualitatively different.

2 Methods

For TRPL studies two types of samples were grown using metal-organic chemical vapor deposition (MOCVD) under identical conditions and subjected simultaneously to electron irradiation. The samples differed only with respect to the active region. In the sample QD1, the latter consisted of one layer of self-assembled InGaAs/GaAs QDs with density $\sim 5 \times 10^{10} \text{ cm}^{-2}$ on a thin wetting layer (WL). Sample CQW contained two coupled InAs/GaAs quantum wells separated by 1 nm. The active layer together with GaAs cladding layers was placed between two $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ barriers. The irradiation by 2 MeV electrons with fluences in the range of 2×10^{15} to $2 \times 10^{17} \text{ cm}^{-2}$ was performed at room temperature using a Van de Graaff accelerator. The TRPL measurements were carried out at 2 K using a single photon counting technique. The exciting Ti^{+} -sapphire laser operated at 790 nm with a pulse width of 2 ps. The time resolution of the detecting system was 30 ps. The averaged excitation density within the pulse was 250 W/cm^2 .

3 Results and discussion

Strong emission bands of QDs (centered at 1.238 eV) and CQW (1.346 eV) were seen in the low temperature cw PL spectra at low excitation densities due to ground state exciton recombination. At the higher excitation densities and/or the higher temperatures contributions from higher-lying QD states and the WL were observed.

With increasing irradiation fluence, all samples exhibited a decrease of the PL intensity. However, whereas in sample QD1 the QD-related PL peak could be observed up to the fluence $1 \times 10^{17} \text{ cm}^{-2}$, the QW-related PL in sample CQW was quenched already between 2×10^{16} and $5 \times 10^{16} \text{ cm}^{-2}$ [7]. This behavior was essentially the same at 10, 77 and 300 K.

The results of the TRPL measurements on QD1 and CQW samples are shown in Fig. 1. The rise and decay times obtained from the exponential fitting are given in Table 1.

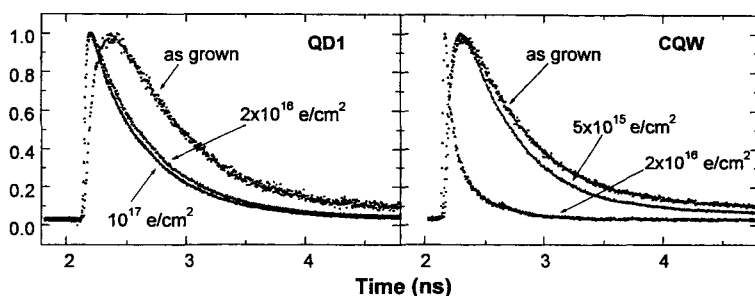


Figure 1. PL transients taken at 2 K of as-grown and electron-irradiated CQW and QD1 samples. Excitation energy is 1.569 eV. Detection energy is 1.230 eV and 1.340 eV for QD1 and CQW, respectively.

Table 1. TRPL rise and decay times.

Sample, fluence (e/cm^2)	τ_r , ps	τ_{d1} , ps	τ_{d2} , ps
CQW, as grown	65	485	-
CQW, 5×10^{15}	50	440	-
CQW, 2×10^{16}	< 20	220	-
QD1, as grown	105	565	-
QD1, 2×10^{16}	< 20	615	295
QD1, 1×10^{17}	< 20	600	230

The transients prior to irradiation can be fitted with single values of the rise (τ_r) and decay (τ_d) times. There is a clear impact of the introduced radiation defects on the rise as well as on the decay times in both CQW and QD samples (Fig. 1). However, there is a striking difference in changes of these times with irradiation. In

CQW sample the PL kinetics still can be fitted with single values of τ_r and τ_d . Both values are reduced obviously due to the shortening of the carrier diffusion length in the barrier and increasing non-radiative recombination in the QW, respectively, caused by the radiation-induced defects. However, in QD sample the PL decay can only be described by at least two different τ_d values: one τ_d characterizes the as-grown sample and another (shorter) one does not change with irradiation dose. We tentatively ascribe this shorter PL decay time constant to the capture of carriers confined in the QDs by defects inside or immediately adjacent to the QDs. Since not all QDs in a sample are disturbed by defects, the slow decay component is still observed even after irradiation. Qualitatively the same behavior has been observed upon resonant (below-bandgap) excitation. However, a poor signal-to-noise ratio and a strong substrate PL impeded a reliable quantitative evaluation. Experiments with other samples are in progress.

4 Acknowledgements

We thank Dr. A. Waughan for performing the electron irradiation. This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) in the framework of Sfb 296 and bmb+f (contract no. 13N7231/7 and CC NanOp) and by Açções Integradas Luso-Alemãs (No. A-14/01). M.G. is grateful to DFG for a Heisenberg grant (Gr 1011/8-1). A.C. acknowledges the grant SFRH/BD/1264/2000 by FCT.

References

1. Bimberg D., Grundmann M., Ledentsov N. N., *Quantum dot heterostructures*, (Wiley, London, 1999).
2. Weisbuch C., Nagle J. In *Science and Engineering of 1D and 0D Semiconductor Systems*, ed. by Sotomayor-Torres C. M., Beaumont S. P., NATO ASI Series B124 (Plenum, New York, 1990) 319.
3. Wellmann P. J., Schoenfeld W., Garcia J. M., Petroff P. M., *J. Electron. Mater.* **27** (1998) 1030.
4. Schoenfeld W. V., Chen C.-H., Petroff P. M., Hu E. L., *Appl. Phys. Lett.* **73** (1998) 2935.
5. Leon R., Swift G. M., Magness B., Taylor W. A., Tang Y. S., Wang K. L., Dowd P., Zhang Y. H., *Appl. Phys. Lett.* **76** (2000) 2074.
6. Sobolev N. A., Cavaco A., Carmo M. C., Grundmann M., Heinrichsdorff F., Bimberg D., *Phys. Stat. Sol.*, March 2001 (in press).
7. Piva P. G., Goldberg R. D., Mitchell I. V., Labrie D., Leon R., Charbonneau S., Wasilewski Z. R., Fafard S., *Appl. Phys. Lett.* **77** (2000) 624.
8. Ribbat Ch., Sellin R., Grundmann M., Bimberg D., Sobolev N. A., Carmo M. C., *Electronics Letters* (in press).
9. Sercel P. C., *Phys. Rev. B* **51** (1995) 14532.

ELECTRIC FIELD EFFECT ON ABSORPTION SPECTRA OF AN ENSEMBLE OF CLOSE-PACKED CdSe NANOCRYSTALS

L. I. GURINOVICH

*Institute of Molecular and Atomic Physics, National Academy of Sciences
220072 Minsk, Belarus*

M. V. ARTEMYEV

*Institute for Physico-Chemical Problems, Belarussian State University
220080 Minsk, Belarus*

U. WOGGON

*Fachbereich Physik, Universität Dortmund
Otto-Hahn-Str. 4, 44221 Dortmund, Germany*

E-mail: leonid@imaph.bas-net.by

Highly monodisperse 1.8 nm CdSe quantum dots were synthesized capped with surface monolayer of 1-thioglycerol. The optical absorption of thin films of matrix free close-packed and isolated in PMMA matrix quantum dots was studied at various electric field biases. The broadening and red shift of optical transitions in close-packed ensemble against the isolated quantum dots are attributed to the formation of collective electronic submini-bands between interacting nanocrystals. The reversible collapse of collective electronic subminibands has been achieved by applying strong electric field to the thin film of close-packed quantum dots.

1 Introduction

Optical properties of II-VI semiconductor nanocrystals are intensively studied and the various observed phenomena are well-described in terms of single isolated quantum dots [1,2]. However, only a few studies exist which deal with collective phenomena in ensembles of interacting nanocrystals. For example, the energy transfer from wide- to narrow-band gap close-packed CdSe nanocrystals has been observed in photoluminescence [3]. First signs for a transition from individual to collective electron states have been obtained by comparing the absorption spectra from ensembles of CdSe nanocrystals of same size but with varying interparticle distance [4]. Isolated CdSe nanocrystals of about 1.8 nm size exhibit a sharp peak in room temperature absorption at 3.25 eV which shows a broadening under increasing the density of close-packed nanocrystals. A theoretical approach based on a statistical analysis of the energy overlap integrals demonstrated a steady increase of the number of delocalized states in the ensemble of interacting quantum dots when the size of the CdSe nanocrystals and the interparticle distance are less than 2 nm and 4 nm, respectively [5]. Delocalization of electron-hole states has clearly been

observed only for highly monodisperse nanocrystals having small electron or hole effective mass. The larger the nanocrystals and the effective masses are, the less is the probability that electron (hole) wavefunctions overlap neighbouring nanocrystals.

In this contribution we present optical properties of close-packed and isolated ultrasmall CdSe nanocrystals using spectroscopic techniques of absorption and electroabsorption. Ultrasmall CdSe nanocrystals are chosen for the following reasons: CdSe has small effective masses for both electrons and holes, the bandgap of CdSe enter the visible range, that simplifies the optical detection. The synthesis of very small, highly monodisperse CdSe nanocrystals of so-called "magic size" is well-established [6]. The obtained results show distinct differences in the optical properties of isolated and close-packed CdSe nanocrystals explained by the existence of delocalized electronic states in an ensemble of interacting semiconductor nanocrystals.

2 Sample preparation

Nearly monodisperse CdSe clusters with average size of 1.8 nm have been synthesized in colloidal solution. Thioglycerol-stabilized CdSe nanocrystals are not soluble in pyridine and precipitate from the solution. The CdSe nanocrystalline phase has been centrifugated, washed twice with methanol and redispersed in a fresh pyridine solution by ultrasonic treatment. Thin films of close-packed CdSe nanocrystals have been prepared by placing a drop of the final colloidal solution onto a quartz glass and drying it. To prepare the thin films of isolated CdSe nanocrystals (~5%) an appropriate amount of polymethylmethacrylate (PMMA) was added to the colloidal solution before drying. The intrinsic absorption of PMMA in the near-UV region is small enough and does not interfere with the absorption of the CdSe nanocrystals.

The CdSe nanocrystals possess a surface stabilizing cap layer of thiol groups strongly bound to cadmium atoms. The replacement of the pyridine surface stabilizing monolayer into a thioglycerol one results in CdSe nanocrystals which are more stable against oxidation and recrystallization.

The average size of the nanocrystals (1.8 ± 0.1 nm) has been determined by fitting the line broadening of X-ray diffraction (XRD) peaks. The measured XRD pattern of the close-packed nanocrystals corresponds to a slightly distorted hexagonal (wurtzite) crystalline structure. A fit of the data with the alternative cubic (sphalerite) structure was not successful. We suppose, these CdSe nanocrystals define their crystalline structure to be a "small piece" of bulk wurtzite rather than molecular.

3 Optical measurements of electroabsorption

A glass plate covered with transparent conductive $\text{SnO}_2\text{:Sb}$ (100 Ohm cm^{-1}) layers has been used as a substrate for electroabsorption measurements. Conducting layers have been prepared by the standard spray pyrolysis of $\text{SnCl}_4\cdot 5\text{H}_2\text{O}:\text{SbCl}_3$ solution on glass slides heated to 600 K. Thin films of both isolated and close-packed CdSe nanocrystals of 250 nm and 100 nm thickness, respectively, were deposited at room temperature as described above. A second, metallic mirror electrode was formed by vacuum evaporation of a 200 nm layer of Al atop the CdSe films. The less than a micron thin $\text{SnO}_2/\text{CdSe}/\text{Al}$ sandwich structure allowed the high internal electrical field with strengths $\sim 10^5 \text{ V cm}^{-1}$ using the external bias below 50 V.

Spectra of electroabsorption were obtained by measuring the beam intensity after passing twice the sample. The incident light passed the glass substrate, the transparent conductive layer, the thin film of CdSe nanocrystals was then reflected back of the Al mirror. The reflected light has been collected under the reflection angle of 20° . The reflexion spectrum of the Al mirror itself is nearly constant in the spectral range of interest. The absorption spectra of both colloidal solutions and thin solid films have been recorded using a CARY 500 spectrometer. The spectral resolution was better than 0.5 nm.

4 Results and Discussion

4.1 Optical absorption

The spectral broadening and the red shift of the discrete optical transitions in the absorption spectra are an indication of delocalization of electronic states in an ensemble of close-packed nanocrystals. Fig. 1 shows the optical absorption of both close-packed and isolated CdSe nanocrystals of same size. Whereas the sample with isolated nanocrystals show the two very pronounced peaks due to discrete absorption of the lowest confined electron-hole pair states, the absorption peaks of the close-packed CdSe-sample are broadened and show the red shift. In particular, the spectral broadening of the second peak is much stronger which can be qualitatively understand within the simple model of a "particle-in-a-box" with finite potential walls. The higher electronic states in the box exhibit a larger extension of their wavefunctions into the barriers. This gives rise to a stronger overlap of the electron (hole) wavefunctions between neighboring nanocrystals. Therefore, the delocalization of the higher energy levels involved in the optical transitions has a much higher probability.

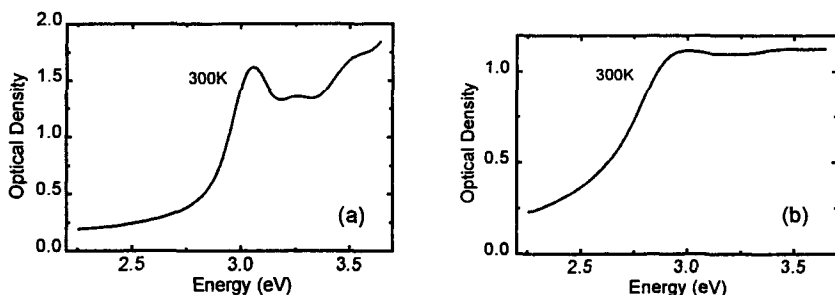


Figure 1. Absorption spectra of thin films of isolated (a) and close-packed(b) CdSe nanocrystals at room temperature.

4.2 Electroabsorption

The application of strong ($10^4 - 10^6$ V/cm) external electrical fields to an ensemble of isolated semiconductor nanocrystals results in the quantum-confined Stark effect (QCSE). The optical transitions are broadened and shifted to the red due to field-induced ionization of excitons [7]. In the case of isolated nanocrystals, the potential wells created by the nanocrystal surface prevent the electron-hole pair dissociation. For ensembles of close-packed, interacting nanocrystals, however, we expect the opposite effect applying an external electrical field. An analogy we know from semiconductor superlattices.

Above a certain applied bias, the band bending can result in a breaking of the minisubband structure and localization of electronic states within the wells. In the thin layers of close-packed nanocrystals the electron states are delocalized over several nanocrystals. With increasing electric field strength, the localization of electronic states in the single nanocrystals should be restored. Hence, the absorption spectrum of close-packed nanocrystals under an external bias should be developed into the spectrum of zero-field isolated nanocrystals. As we demonstrated earlier [4], the formation of delocalized states within an ensemble of close-packed CdSe nanocrystals results in broadening of optical bands and decrease in their intensity. We may expect, that the reverse process of field-induced decoupling of delocalized states will result in an intensity increase of the optical bands.

Fig. 2(a) shows the change in optical density of isolated CdSe nanocrystals under external bias. The measured data for ΔD correspond to broadening and the red shift of the first absorption peak. A careful analysis of the data presented allowed also to resolve the negative signals from the second and third optical transitions at 3.26 eV and 3.47 eV. The peak data coincide with the corresponding energies of the room temperature linear absorption spectrum. In the insert of the peak energy E of the first confined optical transition is plotted versus the squared

external bias U . The nearly linear dependence $E \sim U^2$ is characteristic for the quantum-confined Stark effect.

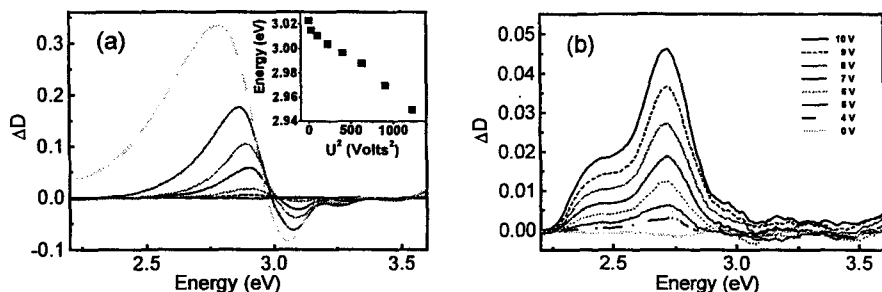


Figure 2. Room temperature Stark signals from thin films of isolated and close-packed CdSe nanocrystals. (a) Change in optical density of isolated nanocrystals at different bias (from top to bottom): 35, 30, 25, 20, 15, 10, 0 V. *Inset.* Energy of first optical band versus squared bias. (b) Change in optical density of close-packed nanocrystals at different bias (from top to bottom): 10, 9, 8, 7, 6, 5, 4, 0 V.

In contrast, the close-packed nanocrystals exhibit only the positive Stark signal with no red shift with increasing electric field (Fig. 2b). Such a positive signal without zero-crossing can not be explained by a broadening of the absorption peak due to field-induced ionization of electron-hole pairs. As a consequence of the decrease in oscillator strength a negative ΔD signal should be observed. For the positive Stark signal, we suggest an increase of absorption because of the stronger localization of the electron-hole pair states, i.e. the reverse effect compared to the delocalization in the close-packed structure. Even when taking into account the more complex behavior of electric field effects (appearance of former forbidden transitions and Franz-Keldysh effect of the delocalized eh -pairs) the observed changes fit well our qualitative picture. The electroabsorption response from both isolated, and close-packed films is fully reversible and initial absorption spectra were restored after the bias was turned off.

5 Conclusions

We compared room temperature optical spectra of isolated and close-packed CdSe quantum dot ensembles in order to proof the existence of delocalized electronic states between interacting ultrasmall dots. The absorption spectra demonstrated distinct broadening and red shift of optical bands in close-packed quantum dot ensemble versus isolated one, which on our knowledge is a result of collective minisubband formation. Using the electroabsorption technique we have shown that collective subminibands in the close-packed ensemble collapsed and primary localization of electronic states can be restored under strong electric field. Further,

we plan to utilize the relatively large electroabsorption response in thin films of ultrasmall CdSe quantum dots for development of large-area electrooptic elements.

6 Acknowledgements

We wish to thank Dr. S. Gaponenko from Institute of Molecular and Atomic Physics for help with discussion of results, Dr. L. Ivashkevich and A. Lyakhov from Belarussian State University for XRD analysis. This work has been supported in part by Volkswagen Stiftung and INTAS research grants.

Reference

1. Woggon U. *Optical Properties of Semiconductor Quantum Dots* (Springer, Berlin, 1997).
2. Gaponenko S. V. *Optical Properties of Semiconductor Nanocrystals* (Cambridge University Press, Cambridge, 1998).
3. Kagan C. R., Murray C. B., Bawendi M. G. Long-range transfer of electronic excitation in close-packed CdSe quantum-dot solids, *Phys. Rev. B* **54** (1996) 8633.
4. Artemyev M. V., Bibik A. I., Gurinovich L. I., Gaponenko S. V., Woggon U. Evolution from individual to collective election states in a dense quantum dot ensemble, *Phys. Rev. B* **60** (1999) 1504.
5. Artemyev M. V., Bibik A. I., Gurinovich L. I., Gaponenko S. V., Woggon U. Formation of collective energy states in a dense ensemble of semiconductor nanocrystals. In *Physics, Chemistry and Application of Nanostructures*, ed. by Borisenko V. E., Filonov A. B., Gaponenko S. V., Gurin V. S. (World Scientific, Singapore, 1999) 83.
6. Ptatschek V., Schmidt T., Lerch M., Müller G., Spanhel L., Emmerling A., Fricke J., Foitzik A.H., Langer E. Quantized aggregation phenomena in II-VI semiconductor colloids, *Ber. Bunsenges. Phys. Chem.* **102** (1998) 85.
7. Colvin V. L., Cunningham K. L., Alivisatos A. P., Electrical field modulation studies of optical absorption in CdSe nanocrystals: dipolar character of the excited state, *J. Chem. Phys.* **101** (1994) 7122.

Ge NANOCRYSTALS IN SiC: AB INITIO SUPERCELL CALCULATIONS OF OPTICAL PROPERTIES

H.-CH. WEISSKER, J. FURTHMÜLLER, F. BECHSTEDT

*Friedrich-Schiller-Universität Jena
Max-Wien-Platz 1, D-07743 Jena, Germany*

E-mail: hcv@ifo.physik.uni-jena.de

Ab initio plane-wave pseudopotential calculations of optical properties of Ge nanocrystals embedded in cubic SiC are reported. Optical matrix elements and band energies are obtained from the PAW method. States within the gap of the host material arise. The spectral properties are calculated using an extrapolative version of the linear analytic tetrahedron method. Due to the interaction between clusters in adjacent supercells the results for a given nanocrystal depend on the supercell size. Moreover, the type of the interface between nanocrystal and host material influences the results considerably. This means that simple two-component effective medium theories cannot fully explain the optical properties of such a composite material.

1 Introduction

Nanometer-sized Ge and Si structures give rise to efficient photoluminescence in the visible up to even the blue wavelength region. This has prompted many studies, exploring both technological applications and fundamental properties. Such nanostructures have been fabricated by ion implantation in amorphous SiO₂ or Al₂O₃ matrices, by electrochemical etching, and by Stranski-Krastanov growth using molecular beam epitaxy [1]. The present contribution investigates properties of such systems using *ab initio* calculations.

Within the VASP package we use density functional theory in local-density approximation and the projector-augmented wave method. Nanocrystals are treated within a supercell approach, thus introducing an artificial translational symmetry. The interaction between adjacent cells can be used to discuss the influence of neighboring quantum dots (QDs) as in self-assembled QD lattices. Host material atoms are replaced shellwise, thus spherical nanocrystals of 1, 5, 17, 41, 83, 147, and 239 atoms are produced. Since the lattice positions are kept, the nanocrystals are highly strained.

2 Results

2.1 Interaction between adjacent supercells

Similar to the case of defects [2], nanocrystals can induce states within the fundamental gap of the host material. This is shown in Fig. 1, visualized by the density of states of a 17-atom Ge nanocrystal embedded in SiC, compared to that of

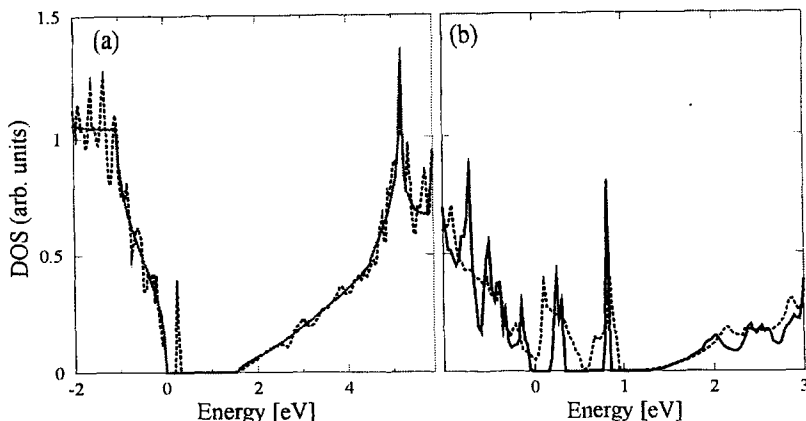


Figure 1. Density of states: (a) 17-atom Ge crystallite in SiC 512-atom cell (dotted) compared to pure SiC (solid), (b) 83-atom Ge nanocrystallite in 512-atom cell (solid) and 216-atom cell (dotted).

host cubic SiC. The states within the gap are three occupied, nearly degenerate ones. These gap-states indicate a type-II heterostructure and influence the optical spectrum. They exhibit a very low dispersion which means that holes in these states are localized at the nanocrystal. Hence, these findings are interesting with regarding a possible breakdown of the k-conservation rules.

The supercell method assumes the interaction between adjacent cells to be negligible. However, this is only approximately fulfilled. Especially when the potential barriers are not very high, as in the case of Ge in cubic SiC, the electronic states are not strongly localized and the interaction between neighboring nanocrystals is large. Therefore, in systems which are not converged with respect to the cell size, the results for the same systems in differently sized supercells differ. While for single nanocrystals localized states show no wave-vector dispersion, due to the artificial translational symmetry dispersion is introduced [2]. This can be seen in Fig. 2. The gap-states induced by the 83-atom Ge cluster are very sharply peaked in the case of the 512-atom supercell while they are - after k-space integrating a "band" of marked dispersion - broadened in the case of the smaller 216-atom supercell.

These effects can also be found in the optical spectra in Fig. 2. The spectra of the 17-atom Ge cluster do not exhibit real differences for the different cell sizes. (The small differences can safely be attributed mainly to the different quality of the

k-space integration method [3]). This can be considered as a demonstration that these results are converged with respect to the cell size. In comparison to that, the spectra of the 83-atom cluster show pronounced differences. Both the overall line shape and the position of the main peak are different.

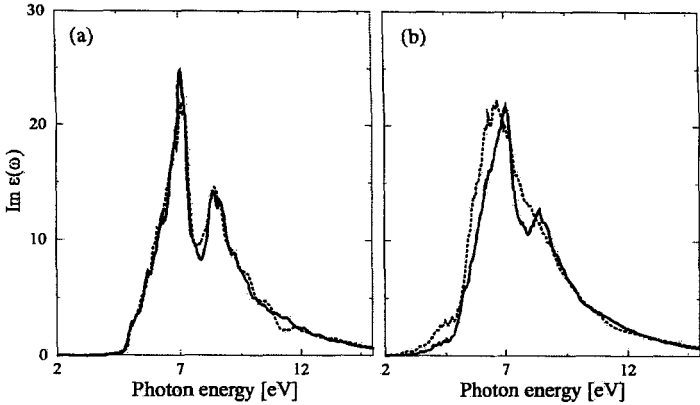


Figure 2. Imaginary part of the dielectric function: (a) 17-atom Ge nanocrystal in SiC, (b) 83-atom Ge nanocrystal. The two supercell sizes 512 (solid line) and 216 (dotted) are compared.

2.2 *Validity of effective medium theories*

Effective medium theories are used to calculate the optical properties of composite systems in terms of relative fractions, filling factors, and the like. Therefore the question arises if they can be related to the results of our calculations. In Fig. 3(a)

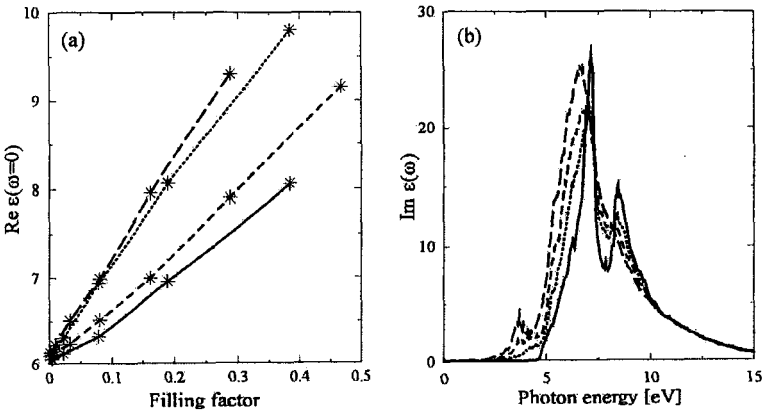


Figure 3. (a) Dielectric constant versus filling factor for: 216-cell, Ge-C interface (solid), 216-cell, Ge-Si interface (dotted), 512-cell, Ge-C interface (dashed), 512-cell, Ge-Si interface (long-dashed). (b) Imaginary part of dielectric function for nanocrystals of 1(solid), 83(dotted), 147(dashed), and 239 (long-dashed) atoms, Ge-C interface, 512-atom supercells.

we consider the static dielectric constant for four different situations: two different interfaces between the Ge cluster and the host material are treated, viz. Ge-C and Ge-Si, both in 216 and the 512-atom cells. If a simple two-component effective medium theory as a function of the filling factor was to explain the results, all the curves in Fig. 3(a) had to coincide. The fact that this is obviously not the case can be traced back to both the interaction influence of the cell size, and interface effects.

2.3 Overall spectra $\epsilon(\omega)$: Ge

The imaginary part of the dielectric function of spherical Ge nanocrystals in cubic SiC is shown in Fig. 3(b). The interface is Ge-C in all cases. One observes a significant deviation of the spectra from the behavior of pure SiC with increasing size of the nanocrystals. There is a reduction of the high-energy SiC peak located at about 8.4 eV in the DFT-LDA spectrum with mixed E'_1 , E'_0 , and $E_2 + \delta$ character. The lower-energy peak shows a similar, but much weaker influence of the nanocrystal due to its E_0 and E_1 character. On the other hand, below 3 eV an additional shoulder occurs. Its development is accompanied by a red-shift. It seems that this shoulder corresponds to the E_1 structure in unstrained Ge. The shifts of the energy peaks with changing dot size do not follow the common rules of spatial quantization. We trace the weak influence of the dot size back to the type-II heterostructure behavior.

Optical properties of the considered systems are determined by the dielectric function. However, in particular the luminescence is determined by the lowest unoccupied and the highest occupied states, i.e., in the Bloch electron language, the band edge states and the states within the gap. It is for this reason that we have also presented the density of states of our nanocrystal systems.

In conclusion, germanium nanocrystals in cubic SiC have been studied. Both the density of states and the dielectric function show the influence of the dot material and the effects of spatial quantization. Due to the different interface effects and the interaction between neighboring nanocrystals in the supercell approach it has been demonstrated that simple two-component effective medium theories cannot account for the behavior of our systems. The optical spectrum of the Ge nanocrystals has been discussed.

References

1. Fissel A., Pfennighaus K., Richter W., Investigations of Stranski-Krastanov growth kinetics of Si-dots on 6H-SiC(0001), *Appl. Phys. Lett.* **71** (1997) pp. 2981-2983.
2. Zywiets A., Furthmüller J., Bechstedt F., Vacancies in SiC: Influence of Jahn-Teller distortions, spin effects and crystal structure, *Phys. Rev. B* **59** (1999) pp. 15166-15180.
3. Weissker H-Ch., Furthmüller J., Bechstedt F., *Phys. Rev. B*, to be submitted.

SURFACE ENERGIES OF Ge AND Si AND CONSEQUENCES FOR NANOCRYSTALLITES

A. A. STEKOLNIKOV, J. FURTHMÜLLER, P. KÄCKELL, F. BECHSTEDT

*Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität
Max-Wien-Platz 1, 07743 Jena, Germany*

E-mail: andrey@ifo.physik.uni-jena.de

Formation of nanocrystallites and determination of their equilibrium shapes are discussed using Wulff construction and absolute surface energies depending on orientation. Energetics is studied considering the low-index surfaces (111), (110), and (100) of Ge and Si with different reconstructions such as (1x1), c(4x2), c(2x8), and (7x7) using an *ab initio* plane-wave-pseudopotential code. Examples of Ge nanocrystallites are.

1 Introduction

The absolute value of the surface free energy of a crystalline solid is one of the most important fundamental quantities which characterizes a large number of basic phenomena. Among them there are crystal growth, surface faceting, growth of thin layers, and shape of small crystallites. One of the fascinating problems concerns the equilibrium shape of nanocrystallites fabricated from group-IV materials Ge and Si. The formation of self-assembled islands, or quantum dots, during the epitaxial growth of Ge on Si(100) [1] and Si on α -SiC(0001) [2], is characterized by several distinct island shapes and an unusual size distribution.

The most obvious problem in this field is that of determining what shape a small crystal must assume if its surface free energy is to be a minimum for a given volume. The solution could be found using the Wulff theorem. The surface free energy of any crystal is an integral of the form

$$\int \gamma(n) ds,$$

where γ is the surface free energy per area as a function of the orientation $\mathbf{n}$. In contrast to liquids, crystals have nontrivial equilibrium shapes because the surface energy depends on the orientation of the surface relative to the crystallographic axes of the bulk. Thus, for a macroscopic or mesoscopic crystal, bounded by oriented surfaces, the Wulff construction could be used for finding the equilibrium crystal shapes having the minimum surface free energies.

The determination of the surface free energy is another problem. There are only a few experimental data because they are difficult to measure. Theoretical data are also rather rare. The fully quantum-mechanical treatment gives usually only relative surface energies for different reconstructions but one and the same

orientation. The calculations are mainly restricted to semi-empirical methods as the tight-binding approach [3] or the application of classical interaction potentials [4]. In this paper we present *ab initio* calculated surface energies for low index surfaces of Si and Ge and discuss the Shapes of crystals based on these surfaces.

2 Methods

The total energies are calculated within the density functional theory (DFT) and the local density approximation (LDA). Explicitly we use the VASP code [5]. The electron-ion interaction is treated by non-normconserving ultrasoft pseudopotentials of the Vanderbilt type [6]. The electron-electron interaction is described by the Ceperley-Alder functional as parametrized by Perdew and Zunger. As a consequence the cutoff for the plane-wave expansion of the single-particle eigenfunctions are restricted to 9.6 Ry (Si) and 8.8 Ry (Ge). Our calculations employ the conjugate-gradient method to minimize the total energy of the system with respect to the atomic coordinates $\{\mathbf{R}_i\}$. When the Hellmann-Feynman forces are smaller than 10 meV/Å, the surface structure is considered to be in the equilibrium. The lattice constants a and fundamental energy gaps E_g are $a = 5.398$, 5.627 Å, and $E_g = 0.46$, 0.00 eV within DFT-LDA.

To model various surfaces we consider a periodic arrangement of slabs along the surface normal. Each slab consists of a certain number of atomic layers, which are separated by vacuum regions. It contains 8 atomic layers and a vacuum region equivalent in thickness to 10 atomic layers in the case (111) and (100) surfaces but 15 atomic layers plus 9 atomic layers of vacuum in the case (110) Si and Ge surfaces. The bottom of each slab is saturated by hydrogen to imitate the bulk. The first 5 topmost layers are allowed to relax.

3 Results and discussions

In Table 1 the absolute surface energies of unrelaxed and the energetically lowest reconstructions for Ge and Si are presented.

According to our calculations we find the most favorable Ge and Si surfaces and their reconstructions. It is 7×7 (dimer-adatom-stacking fault model) [7] in the case of silicon (111) and $c(2 \times 8)$ adatom reconstruction [8] for germanium (111), which is in agreement with experimental data. (110) surfaces, where no reconstruction is allowed show buckled chains. In the case of (100) surfaces, the $c(4 \times 2)$ buckled dimer model [9] is the most favorable one. In this paper we do not present other calculated characteristics of the considered surfaces, such as geometry parameters and band structure, neither for stable nor for metastable reconstructions.

Table 1. Absolute surface energies of low-index Ge and Si surfaces per unit area.

Orientation	Reconstruction	γ (J/m ²)	
		Si	Ge
(111)	unrelaxed	1.84	1.35
	c(2x8)		1.02
	7x7	1.22	
(110)	unrelaxed	2.15	1.54
	relaxed	1.81	1.20
(100)	unrelaxed	2.42	1.76
	c(4x2)	1.43	1.07

Using the idea, that the shape of a nanocrystal can be nearly described by that of a macroscopic one bounded by crystallographic facets, it is possible to construct crystallite shapes by polyhedra with low-index surfaces. In Fig. 1 possible resulting pyramids oriented in [100] or [111] direction are presented. The third pyramid shows that it is necessary also to consider other surfaces (e.g. (221)) and determine their absolute surface energies. We have to mention that these pyramids may be cut perpendicular to their orientation and, hence, change into domes.

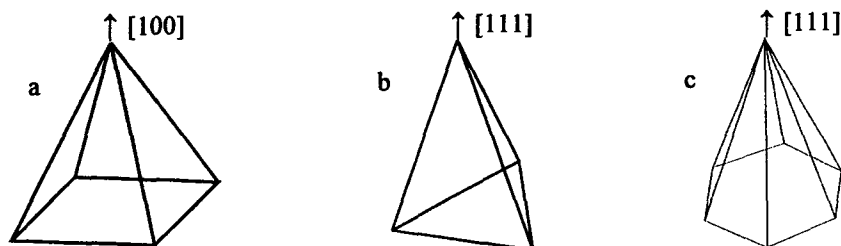


Figure 1. Possible pyramids: square-based bounded by (110) surfaces (a); triangle-based bounded by (100) surfaces (b); hexagon-based bounded by (100) and (221) surfaces (c).

Having the model of crystal shapes and absolute surface energies we can optimize their absolute crystallite energies and derive the equilibrium shape for a given volume V . Fig. 2 shows that the energy behavior depends on size. This is presented for two Ge nanocrystal pyramids. In both cases, the critical point, where the characteristic basis length is becoming close to equilibrium one is 15-20 nm. Usually (it is not shown in Fig. 2) cutting of the pyramids gives rise to a lower total energy because of the energetical ordering $\gamma(111) < \gamma(100) < \gamma(110)$. This tendency is in agreement with experimental findings [10].

In conclusion, we plan to study the shape of the pyramids in more detail within the model described above. In particular, we plan to discuss the shape dependence on the height of the pyramids, the saturation of the surface bonds, the inclusion of more facets, and growth. The effect of the strain field in the nanocrystallites induced by the substrate or the wetting layer is simulated within the macroscopic elasticity theory.

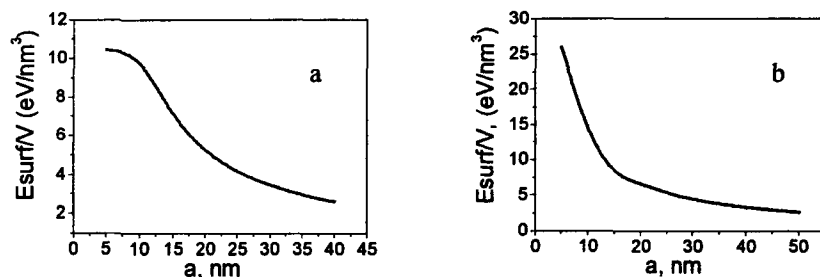


Figure 2. Surface energy divided by volume of simple square-based (a) and triangle-based (b) Ge pyramids versus the edge length a of the pyramid basis.

References

1. Eaglesham D. J., Cerullo M., Dislocation-free Stranski-Krastanov growth of Ge on Si (100), *Phys. Rev. Lett* **64** (1990) pp.1943-1946.
2. Fissel A., Pfennighaus K., Richter W., MBE growth of quantum-size Si-dots on SiC(0001) monitored by RHEED, *Thin Solid Films* **318** (1998) pp.88-92.
3. Wilson J. H., Todd J. D., Sutton A. P., Modelling of silicon surfaces: a comparative study, *J. Phys.: Condens. Matter* **2** (1990) pp.10259-10288.
4. Gilmer G. H., Bakker A. F., Molecular dynamic simulation of steps at crystal surfaces, *Mater. Res. Symp. Proc.* **209** (1991) pp. 135-145.
5. Kresse G., Furthmüller J., Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54** (1996) pp. 11169-11186.
6. Furthmüller J., Käckell P., Bechstedt F., Kresse G., Extreme softening of Vanderbilt pseudopotentials: General rules and case studies of first-row and d -electron elements, *Phys. Rev. B* **61** (2000) pp. 4576-4587.
7. Brommer K. D., Needels M., Larson B. E., Joannopoulos J., *Ab initio* theory of the Si(111)- 7×7 surface reconstruction: a challenge for massively parallel computation, *Phys. Rev. Lett.* **68** (1992) pp. 1355-1358.
8. Tackeuchi N., Selloni A., Tossatti E., Do we know true structure of Ge(111)c(2x8), *Phys. Rev. Lett.* **69** (1992) pp. 648-651.
9. Needels M., Payne M. C., Joannopoulos J. D., *Ab initio* molecular dynamics on the Ge(100) surface, *Phys. Rev. Lett.* **58**, (1987) 1765.
10. Ross F. M., Tromp R. M., Reuter M. C., Transition states between pyramids and domes during Ge/Si island growth, *Science* **286** (1999) pp. 1931-1934.

2D NANOSTRUCTURES AND 3D SILICIDE NANOCRYSTALLITES AT RARE-EARTH METAL/Si(111) INTERFACES: FORMATION MECHANISM AND PROPERTIES

T. V. KRACHINO, M. V. KUZ'MIN, M. V. LOGINOV, M. A. MITTSEV

*A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences
Polytechnicheskaya 26, 194021 St. Petersburg, Russia*

E-mail: M.Kuzmin@pop.ioffe.rssi.ru

The mechanism of rare-earth metal/Si(111) interface formation is found to be similar to the Stranski-Krastanov type within a wide range of temperatures. The properties of both 2D ordered nanostructures and 3D rare-earth silicide nanocrystallites are studied. Some results (thermal stability, work function, the binding energy of RE atoms in 2D domains and 3D silicide islands) are discussed for the first time.

1 Introduction

In this paper we will discuss some results which were obtained in the study of the thin-film structures grown by rare-earth (RE) metal deposition onto Si(111) surface. The silicides formed at RE/Si interfaces possess outstanding physical and chemical properties [1,2]. Therefore, these systems are of interest in both fundamental and applied aspects. In spite of the electronic structure of given interfaces was widely characterised in previous studies [1,2], the information about their thermal stability, binding energies, work function was not obtained. For this reason the growth mechanism involved still under discussion. In this paper we present the abovementioned data obtained within a wide temperature range for three systems: Eu/Si(111), Yb/Si(111), and Sm/Si(111).

2 Experimental

The experiments were performed in the ultra-high vacuum (UHV) chamber with the base pressure 6×10^{-11} Torr by thermal desorption spectroscopy (TDS), isothermal desorption spectroscopy, low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), work-function measurements, and mass spectrometry. Both 2D nanostructures and 3D silicide nanocrystallites were obtained by two different means: (i) RE metals were deposited onto Si substrate at room temperature followed by annealing at 600-1140 K and (ii) deposition was done onto Si substrate heated up to the same temperatures. Other experimental details could be found in our previous paper [3].

3 Results and discussion

3.1 The mechanism of RE/Si(111) thin-film structure formation

We established that the growth mechanism of the systems studied is similar in a wide range of temperatures to the Stranski-Krastanov type. At first, the 2D ordered film, or the wetting layer, is found to form on Si within the adsorption stage. Then, this stage is followed by the growth of 3D nanocrystallites of RE silicide. It should be especially emphasized that in earlier attempts to establish the formation mechanism of RE/Si systems their characterisation was performed at room temperature, while the results of the present study were obtained immediately within a wide range of temperatures, including temperatures at which technological processing is usually performed.

The best illustration of such mechanism is TDS results. In the case of Eu/Si system, the TD spectra shown in Fig. 1 include several peaks. There is a principal

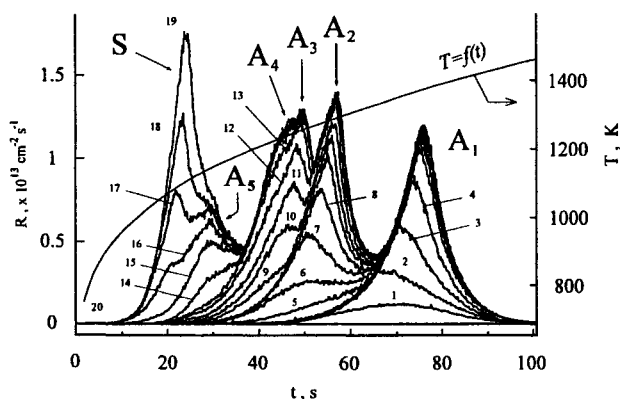


Figure 1. TD spectra of Eu/Si(111) system for different initial concentration of Eu atoms ($1 \text{ ML} = 7.84 \times 10^{14} \text{ at/cm}^2$): 1–0.04, 2–0.08, 3–0.12, 4–0.16, 5–0.20, 6–0.24, 7–0.28, 8–0.32, 9–0.36, 10–0.40, 11–0.45, 12–0.49, 13–0.53, 14–0.57, 15–0.61, 16–0.65, 17–0.69, 18–0.73, 19–0.77 ML. The peaks A_1 – A_5 correspond to Eu desorption from 3×2 , 3×1 , 5×1 , 7×1 , and 2×1 nanocrystals, respectively (see section 3.2). The peak S is due to Eu evaporation from 3D silicide nanocrystallites. Also shown is the silicon crystal temperature T plotted against heating time t (curve 20).

difference between the high-temperature peaks A_1 – A_5 and the peak S appeared at the lowest temperature. The formers are found to be caused by Eu desorption from 2D nanocrystals of the wetting layer, while the latter is due to Eu evaporation from 3D silicide nanocrystallites. The TD spectra led us also to the important conclusion that Eu silicide crystallites are thermally less stable than the 2D layer. But, at the same time, Eu silicide crystallite formation is energetically more preferable than the growth of bulk metallic film. For this reason the latter can exist as a metastable phase only at room temperature. In the case of Yb/Si system, TD spectra are very

similar [4]. But, in the case of Sm/Si system, all peaks are overlapped strongly in TD spectra [5]. It is connected to much higher reactivity of Sm. For this reason the onset of formation of 3D silicide nanocrystallites occurs at the Sm/Si interface before the 2D adsorbed film is filled completely.

Based on the above results, it is naturally to conclude that the investigation of systems considered should be separated into two different parts: 2D film formation and 3D growth of silicide nanocrystallites.

3.2 Adsorption stage

The comparison of TDS and ITDS results with our data obtained by LEED revealed that the wetting layer consists of 2D nanocrystals whose structure depends strongly on the amount of RE atoms deposited onto Si surface. At low concentration $N \leq 1.1 \times 10^{14}$ at/cm² the nanocrystallites with the 3x2 unit cell grow. Their structure is coordinated with that of the underlying silicon layer. The increase of RE concentration results in rising of the surface area occupied by 3x2 nanocrystals. When these islands cover the Si surface entirely, the structure of 2D layer starts to be more compact. The further growth demonstrates also the islanding behaviour, i.e. the formation of 3x1 nanocrystals occurs. The atomic arrangement of RE atoms in these islands is shown to be coordinated with the structure of Si surface as well, but the atomic density in 3x1 unit mesh is higher than that in 3x2 structure. The process of transformation of nanocrystallite structure continues until the clusters with the densest atomic arrangement are formed for the given RE/Si(111) system. All 2D nanostructures exhibit very high thermal stability. We observed the corresponding LEED patterns directly at so high temperatures that RE atoms started to evaporate from these domains into vacuum.

Physical properties of 2D nanocrystallites such as thermal stability, binding energies of RE atoms, activation energies of 2D sublimation, and the work function were studied. These investigations showed that the growth of these structures is thermally activated process. The growth is also suggested to be accompanied by reconstruction of upper Si layer under the nanocrystals and, hence, may be considered as one of constituents of self-organisation. The Si layer reconstruction may involve formation of polarised Si-Si dimers of silicon atoms not bonding to RE atoms and lead to appearance of charge density waves on the surface.

3.3 Silicide-formation stage

The growth of Eu and Yb silicide nanocrystallites is found to occur always on the continuous wetting film formed by 2D nanocrystals with the most close-packed 2x1 structure at concentration $N \geq 3.9 \times 10^{14}$ at/cm² [3,4]. In the case of Sm silicide, the 3D crystallites begin forming on the 2D film with less close-packed structure at $N < 3.1 \times 10^{14}$ at/cm² [5].

Within the talk at the Conference we will also report for the first time on thermal stability, evaporation mechanism, work function, and atomic structure of RE silicide nanocrystallites. RE silicides demonstrate considerable thermal stability and decompose completely at high temperatures. The metal atoms are found to evaporate as monomers, but Si atoms are incorporated into a crystal lattice of Si substrate. The activation energy for this decomposition increases from Yb silicide (2.9 eV) to Sm silicide (4.1 eV).

According to AES and LEED data, the shape of RE silicide nanocrystallites depends on the substrate temperature at which RE are deposited [6]. The ratio of Eu and Sm silicide crystallite heights to their base area grows as the temperature is increased. This dependence can be used for shape-controlled fabrication of an ensemble of RE silicide nanocrystallites.

References

1. Rossi G., d and f metal interface formation on silicon, *Surf. Sci. Rep.* **7** (1987) pp. 1–101.
2. Netzer F. P., Rare earth overlayers on silicon, *J. Phys.: Condens. Matter* **7** (1995) pp. 991–1022.
3. Krachino T. V., Kuz'min M. V., Loginov M. V., Mittsev M. A., Adsorption stage of the Eu-Si(111) interface formation, *Surf. Sci.* (to be published).
4. Krachino T. V., Kuz'min M. V., Loginov M. V., Mittsev M. A., Initial stages of formation of a Yb-Si(111) interface, *Phys. Solid State* **39** (1997) pp. 224–229.
5. Krachino T. V., Kuz'min M. V., Loginov M. V., Mittsev M. A., Initial stages in the Sm-Si(111) interface formation, *Phys. Solid State* **40** (1998) pp. 341–347.
6. Krachino T. V., Kuz'min M. V., Loginov M. V., Mittsev M. A., Effect of temperature and surface coverage on the samarium interaction with Si(111), *Phys. Solid State* **40** (1998) pp. 1758–1764.

PHOTOLUMINESCENCE OF THE SILICON CARBIDE NANOCCLUSERS EMBEDED INTO POROUS SILICON

A. G. ROZHIN, N. I. KLYUI, V. G. LITOVCHENKO

*Institute of Semiconductor Physics
41 prospect Nauki, 03028 Kiev, Ukraine*

E-mail: rozhin@isp.kiev.ua

YU. P. PIRYATINSKII

*Institute of Physics
46 prospect Nauki, 03022 Kiev, Ukraine*

E-mail: yupiryat@iop.kiev.ua

V. A. MAKARA, O. B. KORNETA

*Kiev National University
4 Glushkova street, 03022 Kiev, Ukraine*

E-mail: kornet@mail.univ.kiev.ua

The effect of rapid thermal annealing upon the properties of porous silicon+silicon carbide film structures is investigated. Significant transformation of the emission bands after rapid thermal annealing is discovered. Models of the observed processes are presented.

1 Introduction

Silicon-based devices take the leading position in the modern electronic market, at least in terms of volume production [1]. Unfortunately, the silicon technology does not cover the branch of ultra-high speed devices and optoelectronics. The main goal of porous-Si research is the realization of efficient light emission devices. The most important fact that prevents applications of porous silicon (PS) is unstable optical parameters. In this connection the most interesting works are directed toward the lowering porous silicon degradation, and studying the luminescence mechanism.

The largest part of research is devoted to stabilization of porous silicon luminescence by different surface processing. Another way to overcome the difficulties with the luminescence aging is the structure creations. The structures of PS+C₆₀ [2], PS+diamond films (or diamond like films) [3,4] have stable efficient luminescence in the visible range of spectra. Unfortunately, these structures have not been used as electroluminescent applications in connection with the difficulties to crease of electrical contacts. The PS+SiC film structure gives opportunity to use outstanding properties of SiC.

2 Experimental

Silicon carbide films were deposited by ion-plasma sputtering of a SiC target in argon-hydrogen atmosphere. A triode system of sputtering was used when plasma discharge was excited by thermoelectric emission and localized as a plane beam by the magnetic field of a permanent magnet. The deposition of SiC on PS was performed in two regimes: (S1) $t_{\text{sub}} = 250$ C $\tau = 60$ s, $U_{\text{sput}} = 1000$ B, $U_{\text{bv}} = 100$ B, $I = 1$ A; (S2) $t_{\text{sub}} = 280$ C $\tau = 120$ s, $U_{\text{sput}} = 1000$ B, $U_{\text{bv}} = 100$ B, $I = 1$ A. Thickness of the SiC films measured by laser ellipsometer was: 80 and 200 nm for S1 and S2, respectively. The samples with PS and PS+SiC were subjected to rapid thermal annealing (RTA) in an argon environment (1100 K, 30 s).

Photoluminescence (PL) was excited by N_2 laser ($\lambda_{\text{ex}} = 337.1$ nm, $\tau = 10$ ns, $P = 5$ kW). For detecting time resolved PL the stroboscopic registration system was used. That gives the possibility to attain the maximum temporal resolution.

3 Result and discussion

Fig. 1 shows the integral (1 - 3) and nanosecond (4 - 6) PL spectra of PS and PS+SiC structures. The spectrum of initial PS has a peak at 680 nm (curve 1), and wide band with a maximum at 450 nm and shoulder near 600 nm in the nanosecond spectra (curve 4). Deposition of thin (~ 80 nm) SiC films (S1) on the surface of PS resulted in decreasing of PL intensity in the longwave range and the spectral upshift of the PL maximum. A new band of blue light emission (curve 2) appears that probably caused by Si-C complex creation [5,6]. This assumption is confirmed by the nanosecond spectrum (curve 5) of S1, which has the strong PL band near 450 nm. The more significant effect of the SiC film on the PL of PS has been observed for the S2 series. In this case, the blue emission is only presented in integral (curve 3) and nanosecond (curve 6) PL spectra. The difference in PL spectra for S1 and S2 series can be explained by SiC film thickness. When the thin film (~ 80 nm) was deposited, SiC penetrated into PS layer and created carbon based compounds. For the thicker deposited film the SiC layer is located on the surface (S2 samples) and the blue luminescence of S2 can be interpreted by 3C-SiC emission.

Fig. 2. shows integral (1 - 3) and nanosecond (4 - 6) PL spectra of the samples subjected to RTA.

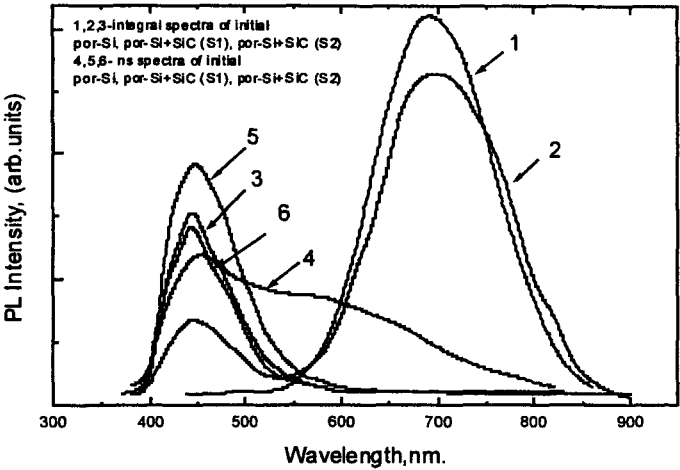


Figure 1. PL spectra of as-fabricated PS and PS+SiC film structures. Intensities are changed for convenience: 3- 1 x 3; 1- 1/3 times.

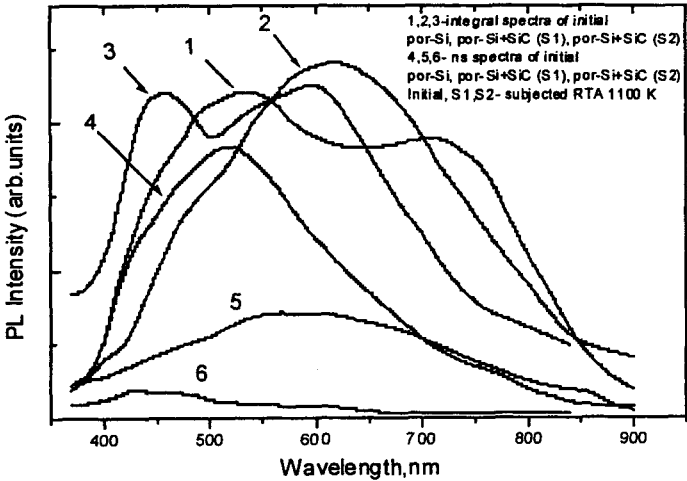


Figure 2. PL spectra of PS, PS+SiC film structures subjected to RTA. Intensity of the spectrum 2 is decreased 6 times.

The RTA treatment brings the substantial decrease of PL intensity (~25 times) in comparison with initial samples and considerable variation of spectral bands. The integral spectrum of PS (curve 1) show two bands: 720 and 540 nm. The band at 720 nm is associated with the emission from deep porous layers (quantum wire of large diameter) and caused by the long-lived component of luminescence [7]. The shortwave band can be interpreted with the short-lived component from the modified near-surface quantum wires [9]. The nanosecond PL spectrum (curve 4) of initial PS has confirmed the origin of the shortwave band in the integral spectra. The spectrum of PS+SiC (S1) and (S2) (curve 2, curve 3) after RTA treatment show the wide band with a maximum at 600-650 nm and emission at 450 nm. The light intensity from the S1 annealed sample is six times larger as compared with initial PS subjected to RTA. Strong upshift (~ 100 nm) is observed with respect to the initial PS+SiC sample. Clustering processes with participation of SiC in quantum wires cause these spectral changes, increasing the probability of radiative transitions from the upper energy level. This assumption is confirmed by PL kinetics for samples before and after RTA (not presented). The emission at 450 nm (curve 2 and curve 3) resulted from the presence of 3C-SiC compounds. This band is more pronounced for S2 than for S1 due to the SiC layer on the surface.

References.

1. Hamilton B., Porous silicon, *Semicond. Sci. Tehnol.* **10** (1995) pp. 1187-1207.
2. Feng Yan, Xi-mao Bao, Xiao-wei Wu, Photoluminescence spectra of C₆₀ molecules embedded in porous Si, *Appl. Phys. Lett.* **67** (1995) pp. 3471-3473.
3. Obratsov A. N., Pavlovsky I. Yu., Timoshenko V. Yu., CVD Diamond growth on porous Si. In *Diamond & Diamond-Like Film Applications* (Technomic publishing Co., 1998).
4. Piryatinskii Yu. P., Semenov V. A., Klyui N. I., Rozhin A. G., Diamond-Like Film-Porous Silicon Systems: New Approach for Optoelectronics Devices Fabrication, *J. Chem. Vapor Depos.* **5** (1997) pp. 207-212.
5. Xing-Long Wu, Feng Yan, Xi-Mao Bao, et al., *Appl. Phys. Lett.* (1996) pp. 2091-2093.
6. Rozhin A. G., Klyui N. I., Piryatinskii Yu. P., Semenov V. A. Photoluminescence porous Si- diamond like carbon film structures subjected to rapid thermal annealing, *Tech. Phys. Lett.* **25** (1999) pp. 304-306.
7. Kompan M. E., Shabanov I. Yu., Beklemyshev V. I. et al., *Fizika i Tekhnika Poluprovodnikov* **30** (1996) 1095 (in Russian).

EXCITON RECOMBINATION MECHANISM IN LIGHT EMITTING NANOCRYSTALLINE SILICON

A. V. SACHENKO, E. B. KAGANOVICH, E. G. MANOILOV

*Institute of Semiconductor Physics NAS of Ukraine
45 prosp. Nauki, 03028 Kyiv, Ukraine*

E-mail: ebk@l-dif.semicond.kiev.ua

We investigated photoluminescence of nanocrystalline silicon in the visible range at room temperature within the framework of two effects: quantum size and dielectric amplification. The estimates of exciton binding energies E_{exc} showed that in the case of small quantum dots in vacuum these energies could be ~ 1 eV. It is a reason to consider an exciton recombination share to be large. The auger excitonic recombination was considered as well. It is shown that observed phenomena can be explained with excitonic recombination mechanism besides band-to-band recombination of free charge carriers.

1 Introduction

Starting with the work by Canham et al. [1] an association between photoluminescence (PL) of porous silicon (por-Si) and emitting annihilation of excitons was considered (see, e.g. [2]). Even in the earlier work by of Keldysh et al. [3], it was shown that in low-dimensional semiconductor composite structures excitons possess a large E_{exc} value both due to the quantum confinement (QC) and the dielectric amplification effect (DAE). The latter can appear since Si nanocrystals (NC) are immersed into a medium with the lower dielectric permeability, ϵ_2 , than that of Si, ϵ_1 ($\epsilon_2 < \epsilon_1$). This work is also aimed at revealing excitonic mechanisms of visible PL in NC-Si.

2 Method of measurements and samples

We compared PL properties for a wide set of NC-Si samples, namely: from silicon oxide films enriched with silicon up to traditional layers of por-Si through several intermediate states of structures containing Si NC of different sizes in SiO_x matrix with various porosity and composition. Two types of NC-Si films prepared by pulse laser evaporation of c-Si in vacuum were used. The first type of the films was deposited using a direct particle flow from an erosion flame onto a substrate disposed at some distance along the perpendicular from the target. The second type was deposited from a reverse particle flow onto a substrate disposed in the plane of the target [4]. Time-resolved PL was excited by a nitrogen laser ($\lambda = 337$ nm, $\tau = 8$ ns), and signal was registered in the photon counting mode.

3 Results of time-resolved PL measurements

Our analysis of correlation between time-resolved PL characteristics and structure features of investigated samples showed that PL properties of the first type films and por-Si represent two limiting cases, namely: the first displays PL properties of structures containing Si NC in the form of quantum dots embedded into SiO_x with minimum porosity ($p \approx 1-2\%$). Their PL was characterized by only fast ($\tau < 50$ ns) PL component in the range of energy 1.6-3.2 eV. With reducing NC sizes (d), an PL intensity arose, and its emission peak shifted towards blue part of the spectrum.

The second limiting case corresponds to PL properties of por-Si. These are due to structures in the form of quantum wire in a matrix of very porous SiO_x ($p \approx 70-85\%$). Along with the fast component, their PL contained the slow one with relaxation times reaching several milliseconds. The latter dominates, its spectrum being shifted to the low-energy side (1.6-2.1 eV).

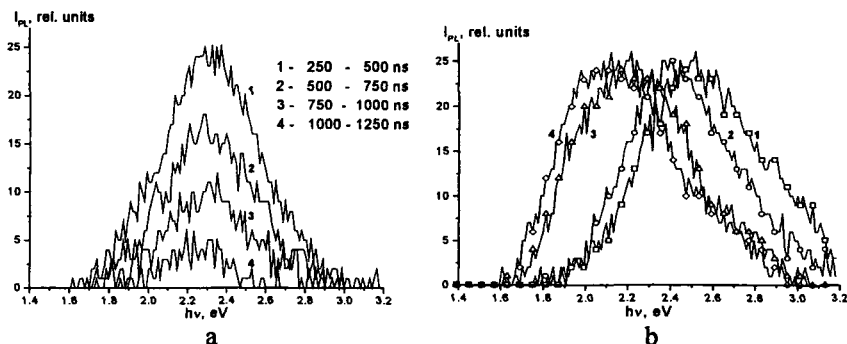


Figure 1. Time-resolved PL spectra for the second type films: a – aged in air, $T = 300$ K; b – for 4 samples: 1 – as-grown, 2 – aged in air, 3, 4 – annealed at 600°C and 1000°C , respectively. $T = 90$ K, $\tau < 250$ ns.

Between these limiting cases, we observed PL properties of the second type films that contained Si NC in the form of quantum dots with various size in the matrix of intermediate porosity ($p \sim 30-50\%$). As-prepared samples of the second type had more intensive PL than samples of the first type, but its spectrum contained only the same fast component. With reducing d , its PL spectrum maximum shifted to the blue, PL intensity increased. A slow ($\tau = 50-500$ ns) PL component appeared at $T \approx 150$ K, and its intensity increased with lowering temperature. In the second type samples a contribution of the slow ($\tau > 50$ ns) PL component increased under oxidation. Simultaneously, its relaxation times reached microseconds Fig. 1(a), and the spectrum shifted the low-energy range Fig. 1(b). One can see a correlated decrease of the PL intensity and its relaxation times with temperature above 150 K. PL quantum efficiency reached several percents at 300 K. PL relaxation curves had the shape of stretched exponents similar to por-Si.

4 Discussion of results. Mechanisms of the visible PL

The results obtained can be explained within the framework of the QC model for Si NC. This model is based on the conception that the visible PL occurs due to absorption and emission of photons in NC. Both free charge carriers and excitons in the singlet S and triplet T states can take part in this recombination. Concentration of excitons, n_{exc} , and electron-hole pairs, n , are related by the following expression

$$n_{\text{exc}} = \frac{n^2}{n_0 \exp(-E_{\text{exc}}/kT)}, \quad (1)$$

where n_0 is a statistical factor of the excitonic state, k is the Boltzmann constant, T is temperature. n_{exc} depends effectively on the value of E_{exc} . The value of E_{exc} in nanostructures depends on sizes and shapes of NC as well on matrix dielectric properties. We estimated the dependence $E_{\text{exc}}(d, \epsilon_2)$ for Si NC approximately. The relevant expressions for emission energy of exciton transitions E_{hv} , the band gap shift ΔE_g , and exciton energy E_{exc} can be written as:

$$E_{\text{hv}}(d, \epsilon_2) = E_{g0} + \Delta E_g(d) - E_{\text{exc}}(d, \epsilon_2), \quad (2)$$

$$\Delta E_g(d) = \frac{3\pi^2 \hbar^2}{m_0 F_{\mu c}(d) d^2}, \quad (3)$$

$$E_{\text{exc}}(d) = 13.53 \frac{F_{\mu \text{exc}}(d)}{\epsilon_1^2 (F_e(d))^2}, \quad (4)$$

where

$$F_e(d) \equiv \left(\frac{d}{a_B} \sqrt{\frac{2\epsilon_2/\epsilon_1}{\ln(\epsilon_1/\epsilon_2)}} \right)^{\frac{1}{2}}, \quad (5)$$

m_0 is the electron mass, $\hbar$ is the Plank constant, a_B is the Bohr radius of an exciton in c-Si, $F_{\mu c}(d)$ and $F_{\mu \text{exc}}(d)$ are considered to be similar because of $m_e^* \gg m_h^*$ in small NCs [5].

As seen from Fig. 2, E_{exc} value can be very large reaching 1 eV, the $E_{\text{hv}}(d, \epsilon_2)$ dependence can be gently sloping, more over nonmonotonous.

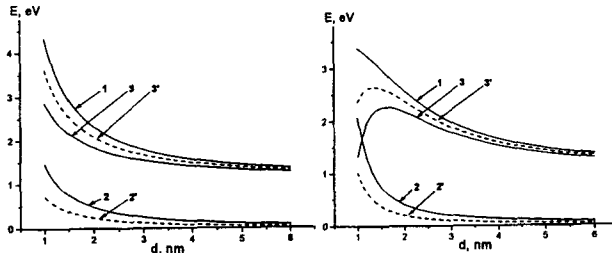


Figure 2. Site dependencies of ΔE_g (1), E_{exc} (2, 2'), E_{hv} (3, 3'), $\epsilon_2 = 1$ (2, 3), $\epsilon_2 = 2.1$ (2', 3'), for fitting function $F_{\mu c}(d)$ from [6] (a) and [7] (b).

References

1. Cullis A. G., Canham L. T., Calcott P. D. J., The structural and luminescence properties of por-Si, *J. Appl. Phys.* **82** (1997) pp. 909–965.
2. Kashkarov P. K., Kamenev B. V., Konstantinova E. A., Efimova A. I., Pavlikov A. V., Timoshenko V. Y., Dynamics of nonequilibrium charge carriers in silicon quantum wires, *Uspehi Fizicheskikh Nauk* **168** (1998) pp. 577–582.
3. Kachanov P. K., Kamenev B. V., Konstantinova E. A., Egimova A. I., Pavlicov A. V., Timoshenko V. Y., Dynamic of nanoequilibrium charge carriers in silicon quantum wires, *Uspekhi Fizicheskikh Nauk* **168** (1998) pp. 577–582.
4. Babichenko V. S., Keldysh L. V., Silin A. P., Coulomb interaction in thin semiconductor and semimetal wires, *Fizika Tverdogo Tela* **22** (1980) pp. 1238–1240 (in Russian).
5. Patrone L., Nelson D., Safarov V. I., Sentis M., Marine W., Giorgio S., PL of silicon nanocrystals with reduced size dispersion produced by laser ablation, *J. Appl. Phys.* **87** (2000) pp. 3829–3837.
6. Hill N. A., Whaley K. B., Theoretical analysis of the geometries of the luminescent regions in por-Si, *Appl. Phys. Lett.* **67** (1995) pp. 1125–1127.
7. Proot J. F., Delerue C., Allan G., Electronic structure and optical properties of silicon crystallites: Application to porous silicon, *Appl. Phys. Lett.* **61** (1992) pp. 1948–1950.
8. Delley E., Stiglmeier E. F., Size dependence of band gaps in silicon nanostructures, *Appl. Phys. Lett.* **67** (1995) pp. 2370–2372.

TIME-RESOLVED PHOTOLUMINESCENCE OF NANOCRYSTALLINE SILICON FILMS OBTAINED BY LASER ABLATION

E. B. KAGANOVICH, E. G. MANOILOV, A. V. SACHENKO, S. V. SVECHNIKOV

*Institute of Semiconductor Physics, NAS of Ukraine
45, prosp. Nauki, 03028 Kyiv, Ukraine*

E-mail: ebk@l-dif.semicond.kiev.ua

Time-resolved visible photoluminescence (PL) of nanocrystalline silicon (nc-Si) films obtained by laser ablation is described and discussed. The PL has the emission spectrum ranging from ~ 1.4 to 3.2 eV with PL relaxation time in the range of 50 ns – 10 μ s. The relation between time-resolved characteristics (intensity, emission spectra, relaxation times, their temperature dependencies) and structural, dielectric properties (size and shapes of Si nanocrystals (NC), oxide phase of NC coating, porosity) were studied. To explain experimental results we consider a PL model in which absorption and emission of photons take place in quantum-sized Si NC. It implies that dynamically coupled subsystems of free charge carries and excitons take part in recombination. Slow (S, $\tau > 50$ ns) band of PL is connected with low-dimensional exciton localized in Si NC. High intensity of nc-Si PL as compared with bulk silicon (c-Si) is determined not only by amplification of a radiative recombination channel, but also by damping of the nonradiative one. It was shown that in the temperature range of 150 - 300 K, relaxation times of PL observed in the range 50 ns- 1 ms were related to nonradiative processes. The mechanisms of nonradiative recombination are considered.

1 Introduction

Although laser ablation technique has been applied for growth of n-Si films photoluminescent in the visible range, for our knowledge, there are no data in literature on results of time-resolved PL measurements of such films. But these measurements can give important information about radiative and nonradiative recombination. In this work such results are presented with the aim to elucidate the nature of visible PL in the nc-Si films.

2 Samples and method of measurement

Films were obtained using pulse laser deposition (laser ablation). The experimental setup contained YAG:Nd³⁺ laser (wavelength 1.06 μ m, pulse energy 0.2 J, duration 10 ns, frequency 25 Hz) and standard vacuum unit. The laser beam was focused in a spot of 500 μ m and scanned the c-Si target. During the deposition, helium or argon was introduced into the chamber. We selected the pressure of gas so that nano-sized particles were deposited back on the target plate. The lighter nano-sized particles were backscattered further from the plume axis (up 15 mm) than the heavier ones

[1]. Thicknesses of the obtained films were 10-150 nm and they decreased with increasing the distance from the expansion axis x . The highest rate of film growth on the target plate was several nanometers per minute. The ellipsometry measurements shown that porosity of these film can reach $p \sim 40-50\%$. Time-resolved PL spectra were measured using the N_2 -laser excitation source (wavelength 337 nm, pulse width 8 ns). The photocurrent signal from a photomultiplier was retrieved by accumulating digitized pulses in a summator.

3 Results

PL of the as-grown films was characterized by only fast ($\tau < 50$ ns) component in the range of emission energy 1.4-3.2 eV. With decreasing NC size PL intensity increased, PL maximum shifted into the blue side. A slow ($\tau = 50-500$ ns) PL component appeared at 150 K and its intensity increased with lowering temperature (Fig. 1(a)). In the course of oxidation a contribution of the slow ($\tau > 50$ ns) PL component increased. Simultaneously, its relaxation times reached microseconds, and PL spectrum shifted into the low-energy range. With rising temperature from 90 to 300 K times showed changes only in the form of a spectrum of the fast component, in particular, in its low-energy range (Fig. 1 (b)).

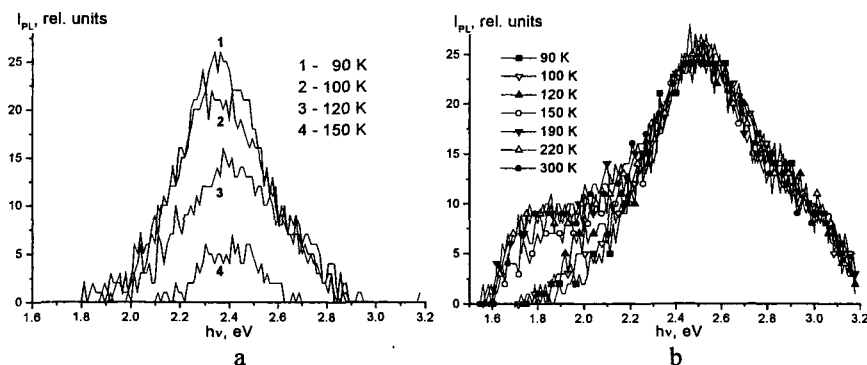


Figure 1. Temperature dependencies of time-resolved PL spectra for as-grown films: a – $\tau = 250 - 500$ ns, b – $\tau < 250$ ns.

We observed the clear correlation between PL intensity rise and increasing time of its relaxation under action of different technological factors, for instance, temperature or thermal treatment time. One can see a correlated decrease of the PL intensity and its relaxation times with temperature above 150 K. A quantum PL efficiency reached several percents at 300 K. PL relaxation curves had the form of stretched exponents like those inherent in por-Si.

4 Discussion of results

As follows from the experiment, time-resolved PL of investigated nc-Si films are characterized by the high quantum efficiency (1-3 %) at room temperatures and cover wide energy (from 1.4 to 3.2 eV) and time (from 50 ns to 1 ms) ranges. Spectrum shapes depend on Si NC sizes, dielectric matrix and conditions of PL measurements, particularly, temperature.

In as-prepared films the observed intensity growth and the spectrum peak shift into the high-energy part with decreasing NC sizes indicates on QE in NC. The broadness of energy spectrum is caused by dispersion of sizes. An increase in the intensity of PL fast component in the low-energy part with temperature from 90 to 300 K (Fig. 1(b)) can be associated with a contribution of radiative transitions including phonons.

Results of the investigations can be explained within the framework of a model based on the conception that the visible PL is due to absorption and emission of photons in NC, and both free charge carriers and excitons in the singlet S and triplet T states take part in this recombination. It was shown [2] that in low-dimensional semiconductor structures excitons possess large binding energies E_{exc} both due to quantum confinement and immersing Si NC into a medium with a lower dielectric permeability, ϵ_2 , than that of c-Si, ϵ_1 ($\epsilon_2 < \epsilon_1$). This is so called dielectric amplification effect (DAE). It is a reason to consider an exciton recombination share to be large in porous nc-Si. The dielectric function decreases during oxidation because of the lower refractive index of SiO_2 compared to that of c-Si. Thus, with oxidation E_{exc} value increases, radiative exciton recombination increases, the exciton transition energy E_{hv} decreases (red shift of PL spectra).

In low-dimensional structures based on indirect-gap semiconductors, radiative lifetimes τ_R are reduced due to weakening of the momentum conservation law, which results in increase of an oscillator strength and a transition probability. Nevertheless, τ_R in nc-Si can reach values up to 10^{-3} s and be equal to those of c-Si. It is obvious thereof that the visible PL efficiency is determined by damping the nonradiative recombination channel in nc-Si as compared to c-Si, where $\tau_{\text{nr}} \sim 10$ ns.

As quantum efficiency values of all investigated samples did not exceed several percents, and a correlated change of PL intensity as well as its relaxation time at $T > 150$ K take place, it follows that the measured PL times are determined by the nonradiative relaxation in this temperature range.

An oxygen diffusion facilitated in pores promotes the passivation of Si-atom dangling bonds and, as a consequence, decrease amount of surface nonradiative levels. The number of these states is more for the large NC than for the smaller ones. Therefore, the damping of the nonradiative surface channel is more efficient in their PL and, accordingly, in more long-wave part of the PL spectrum. This fact explains a red shift of the PL spectrum observed at oxidation as well as PL intensity growth.

There exist estimates of lower limits for surface state densities when at least one local surface state can be present. These are 10^{13} and 10^{10} cm^{-2} for spherical NC with the diameter about 3 nm and wires with dimensions 3 nm x 1 μm , respectively. The above values are usually realized for quantum wires, but for quantum dots it is valid only in the case of very high local density of states. Considering small NC with a low density of surface states and oxidized film samples that have less dimensions and higher passivation levels, we can state that the surface channel of the nonradiative recombination can not be single. When the thickness of the oxide layer grows, the mechanism of the nonradiative recombination associated with charge carrier escaping from NC due to tunneling through potential barriers is hindered [3]. Moreover this mechanism does not agree with the observed temperature dependence of τ_{nr} .

The large values of nonradiative recombination times and non-exponential character of PL relaxation is inherent in the Auger excitonic recombination considered below. Let the exciton concentration exceeds the free charge carries one, and the recombination is determined by exciton energy transfer to a free electron (hole). For this case

$$\tau_{\text{nr}} = \tau_{\text{exc}} \sim \exp(E_{\text{exc}}/3kT)/I^{1/3}, \quad (1)$$

where k is the Boltzmann constant, T is the temperature, and I is an excitation intensity. It follows from (1) that τ_{exc} is great through the large values of E_{exc} in low-dimensional systems. The dependence $E_{\text{exc}}(d)$ determines the set of times τ_{exc} , too. Like E_{exc} , the τ_{exc} magnitude depends on NC sizes, their shape and dielectric properties of the matrix. Moreover, as follows from (1), τ_{nr} increases with E_{exc} increasing. The fact that these τ_{exc} dependencies on the above factors can be observed experimentally testifies to validity of the Auger excitonic recombination mechanism.

References

1. Patrone L., Nelson D., Safarov V. I., Sentis M., Marine W., Giorgio S., PL of silicon nanocrystals with reduced size dispersion produced by laser ablation, *J. Appl. Phys.* **87** (2000) pp. 3829-3837.
2. Babichenko V. S., Keldysh L. V., Silin A. P., Coulomb interaction in thin semiconductor and semimetal wires, *Fizika Tverdogo Tela* **22** (1980) pp. 1238-1240 (in Russian).
3. Vial J. C., Billat S., Bsiery A., Fishman G., Gaspard F., Herino R., Ligeon M., Madeore F., Mihalcescu I., Muller F., Romestain R., Bright visible light emission from electro-oxidized por-Si, *Physica B* **185** (1993) pp. 593-602.

ELECTRON-PHONON COUPLING IN HEAVILY DOPED SILICON

P. KIVINEN, A. SAVIN, A. MANNINEN, J. PEKOLA

*Department of Physics, University of Jyväskylä
P. O. Box 35, FIN-40351 Jyväskylä, Finland*

M. PRUNNILA, J. AHOPELTO

*VTT Microelectronics Centre
P.O.Box 1101, FIN-02044 VTT, Finland*

E-mail: pasi.kivinen@phys.jyu.fi

The coupling constant in electron-phonon interaction is a very important issue in nanoscale applications. We have measured this constant in heavily doped silicon. Electron-phonon interaction is proportional to T^6 and the coupling constant is found to be $1.5 \times 10^8 \text{ W/K}^2\text{m}^3$, which is about one tenth of the value in normal metals.

1 Introduction

Recently microcoolers have been intensively investigated. They provide a promising cooling method for nanoscale devices [1]. Although considerable progress has been made, nanocoolers need improvements for technical applications. One way to improve the cooler is to look for a more effective material. From practical and technological point of view heavily doped silicon is very interesting material for coolers. In this paper we report low-temperature electron-phonon coupling in heavily doped silicon.

2 Theory

A cryogenic refrigeration method, which has been developed during the last years [2], is based on a normal metal/insulator/superconductor (NIS) tunneling. The cooling effect is based on the existence of forbidden energy states within the energy gap, Δ , in the superconductor. Only electrons with energy E higher than the Fermi energy, E_F , can tunnel through an insulating barrier from the normal metal into the superconductor when bias voltage $V < \Delta/e$ is applied across the junction. This cooling therefore cools directly the electrons of the normal metal and the phonon system is refrigerated via electron-phonon coupling.

The heat flow from phonons (temperature T_{ph}) to electrons (temperature T_{el}) is given as [3]:

$$Q_{el-ph} = \Sigma V (T_{el}^5 - T_{ph}^5), \quad (1)$$

where V is the volume of the normal electrode, and Σ is the material-dependent constant [4], which in normal metals is of the order of $10^9 \text{ W/K}^5\text{m}^3$. Recently, electron-phonon interaction at low temperature in a silicon metal-oxide-semiconductor-field-effect transistor has been confirmed experimentally [5].

3 Experiment

Our sample was a silicon-on-insulator structure, in which the heavily doped n-type silicon layer was 53 nm thick. The area of the rectangular sample was $700 \times 100 \mu\text{m}^2$. At helium temperature the square resistance R_{sq} of silicon was 150 Ohm and the Si-Al contact resistance was 40 Ohm. The electron concentration of the sample was $7 \times 10^{19} \text{ cm}^{-3}$. Heating current passed along the long axis of the sample and another perpendicular current was controlled along the short axis for a temperature measurement. One can use an aluminum-silicon contact, which is effectively a NIS-structure, as a thermometer [6], because its I - V characteristic strongly depends on the temperature.

A ^3He dilution refrigerator was used for measurements in the temperature range 100 – 1000 mK. The sample was fixed on a piece of copper, which was connected to another thermometer used for substrate temperature measurements. It was assumed that the phonon temperature was the same as that of the copper holder.

In finding out the electron-photon coupling constant, Σ , we used two different methods. First, we plotted the electron temperature as a function of the heating power and fitted our data using (1) [6]. Another way to approach the problem was considering the slope $(\Delta P/\Delta T)$ of the curve near to $P = 0$ at different temperatures and plot it as a function of T_{ph} . This way we are able to avoid the uncertainty caused by probable overheating of the phonon system in the silicon bar in respect to substrate temperature at high P .

4 Results and discussion

The electron-phonon coupling was measured at different temperatures between 100 mK and 1000 mK. At low temperature the fitting with (1) is nearly perfect. At 300 mK and above the fitting became worse: the dependence of P on T_{el} corresponds to a power lower than 5. This might be due to overheating of phonon system in heavily doped silicon in respect to the substrate.

The electron temperature as a function of power is presented in Fig. 1. The measured curve fitted with (1) is characterized by $\Sigma = 1.5 \times 10^8 \text{ W/K}^5\text{m}^3$. However, there is a noticeable deviation of experimental data from T^5 at low P . The inset in Fig. 1 demonstrates clear minimum in $T_{el}(P)$ about $P = 7 \text{ pW}$. The reason for such peculiar behavior could possibly be the cooling effect. Cooling is very small, but the geometry of the sample is not optimal.

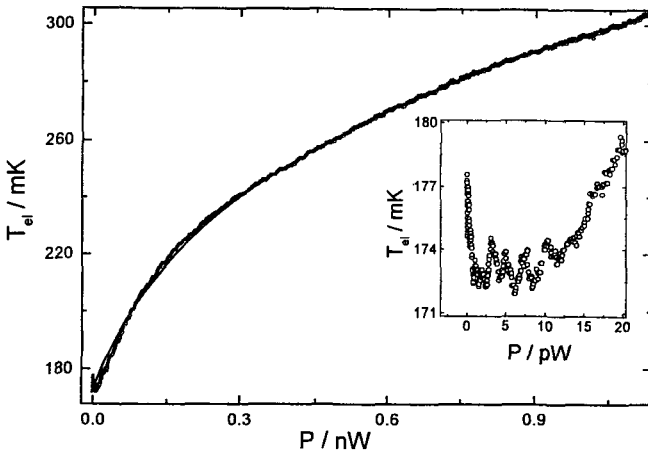


Figure 1. The electron temperature as a function of heating power. The inset is a zoom-out from the beginning of the curve. The solid line corresponds to (1) with $\Sigma = 1.5 \times 10^8 \text{ W/K}^5 \text{ m}^3$.

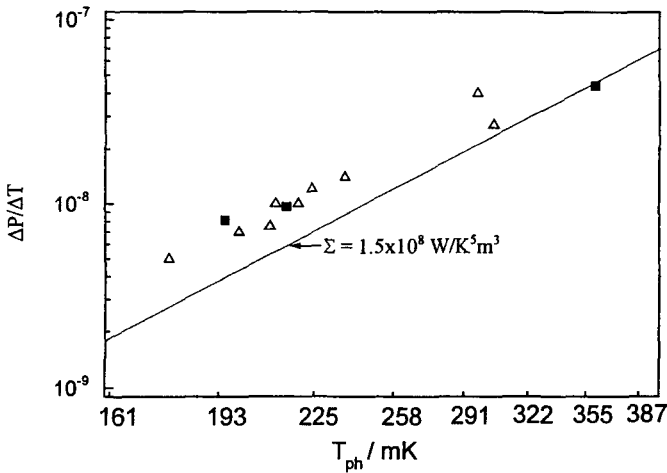


Figure 2. $\Delta P/\Delta T$ versus phonon temperature for two different samples (triangles and squares). The solid line represents the fitted value of Σ from Fig. 1.

As it was mentioned above, another method based on the measurement of derivative of the plot as in Fig. 1, was also used for finding Σ . In Fig. 2 the $\Delta P/\Delta T$ of

the curve is plotted as a function of the phonon temperature in a log-log scale. Open triangles and solid squares correspond to different samples.

The straight line in Fig. 2 corresponds to the derivative calculated from (1) with the value of Σ obtained from the fitting in Fig. 1. All experimental points are shifted upwards with respect to the line. There are two possible explanations for this. The measured $\Delta P/\Delta T$, which differs from dP/dT at $T_{el} = T_{ph}$, makes some error, but the corresponding correction is less than half of the difference.

In conclusion, according to the results obtained, the electron-phonon coupling in silicon is about one tenth of that value in normal metals. This makes silicon very promising material for microcooler applications.

5 Acknowledgments

This work has been supported by Vilho, Yrjö and Kalle Väisälä Foundation, and by the Academy of Finland through projects 46804 and 46805.

References

1. Leivo M. M., Manninen A. J., Pekola J. P., Microrefrigeration by normal-metal/insulator/superconductor tunnel junctions, *Appl. Superconductivity* **5** (1999) pp. 227-233.
2. Manninen A. J., Suoknuuti J. K., Leivo M. M., Pekola J. P., Cooling of a superconductor by quasiparticle tunneling, *Appl. Phys. Lett.* **74** (1999) pp. 3020-3022.
3. Manninen A. J., Leivo M. M., Pekola J. P., Refrigeration of a dielectric membrane by superconductor/insulator/normal-metal/insulator/superconductor tunneling, *Appl. Phys. Lett.* **70** (1997) pp. 1885-1887.
4. Kauppinen J. P., Pekola J. P., Electron-phonon heat transport in arrays of Al islands with submicrometer-sized tunnel junctions, *Phys. Rev. B* **54** (1996) pp. 8353-8356.
5. Zieve R. J., Prober D. E., Wheeler R. G., Low-temperature electron-phonon interaction in Si MOSFETs, *Phys. Rev. B* **57** (1998) pp. 2443-2446.
6. Leivo M. M., Pekola J. P., Averin D. V., Efficient Peltier refrigeration by a pair of normal metal/insulator/superconductor junctions, *Appl. Phys. Lett.* **68** (1996) pp. 1996-1998.

INFLUENCE OF SURFACE PHASES ON ELECTRICAL CONDUCTIVITY OF SILICON SURFACE

D. A. TSUKANOV¹, S. V. RYZHKOV^{1,2,3}, O. A. UTAS^{1,2}, I. A. BELOUS¹,
V. G. LIFSHITS^{1,2}

¹ *Institute of Automation and Control Processes, Russian Academy of Sciences
5, Radio st., Vladivostok 690041, Russian Federation*

² *Faculty of Physics and Engineering, Far Eastern State University
8, Sukhanova st., Vladivostok 690000, Russian Federation*

³ *Core Research for Evolutional Science and Technology
The Japan Science and Technology Corporation
Kawaguchi Center Building, Hon-cho 4-1-8, Kawaguchi, Saitama 332, Japan*

A surface conductivity of the samples with silicon-adsorbate surface phases on Si(100) was measured in ultra-high vacuum by the four-point probe method at room temperature. It is shown that surface phases act as conductive channels. Surface phases Si(100)c(8x2)-Au, Si(100)5x1-Au, Si(100) $\sqrt{2}$ 6x3-Au enhance conductivity of the silicon sample, surface phase Si(100)2x3-Na reduces conductivity, surface phase Si(100)4x3-In has no influence on conductivity. A possible mechanism of the surface conductance is suggested.

1 Introduction

Surface processes in solids (like those in the bulk) are directed towards getting an equilibrium state of the system. "Such states of a substance which can exist simultaneously with each other in equilibrium, while in contact, are *phases* on the substance" [1], i.e. surface processes are directed towards surface phase formation. Surface phases are in thermodynamic equilibrium with the bulk and with other surface phases (if any exist on the surface). Surface phases can be formed by the same atoms as the bulk phases (e.g. Si(100)2x1, Si(111)7x7) or by both substrate atoms and foreign atoms at the surface (e.g. Si(100)2x3-Na, Si(111)4x1-In).

A structure of surface phases is determined by an interaction of atoms with each other and with substrate atoms as well as by the interaction between substrate atoms. Surface phases have their own electronic and crystallographic structure and physical properties [2]. When we deal with a surface phase on a silicon substrate one should explain the electrical transport in the frame of model "two substances which are in contact" (bulk phase and surface phase). In that case instead of term "surface states" which corresponds to "surface" it is necessary to use the term "surface phase's valence band" corresponding to surface in the equilibrium state,

e.g. "surface phase". Electronic states of surface phases (like for "surface states") influence more extensively than the place of surface phases. Due to diffusion and spreading this influence is distributed in the bulk with a penetration depth about one atomic layer.

In the band diagram of the system "a surface phase-substrate" surface phase may have an additional density of occupied states which can enter the silicon valence band as well as it can appear near the Fermi level. The contribution to bulk conductivity will be determined by the distance from these states to the conduction band and by the density of filled states. In such manner charge carriers of surface phase can contribute not only in to conductance of surface phase but also into the bulk conductance.

This is a reason why electrical properties of a surface phase can be studied by the same methods as convenient for bulk solids. Such description of electrical processes in systems "bulk phase-surface phase" makes interpretation of experimental data more simple and understandable. A formed in this manner new two-dimensional material, surface phase, presents additional conducting channel which has essential concentration of charge carriers to contribute in to bulk conductivity. Any destruction of surface phase or displacement it by other surface phase is to have the crucial influence on electrical properties.

Nowadays, semiconductor surface is of great interest for researchers due to strong influence of surface phases on properties of the bulk material. Electrical conduction along the surface in ultra-high vacuum was demonstrated [3-8] to be strongly dependent on the atomic structure of the surface, thus showing that surface phases can noticeably influence electronic properties of silicon substrate.

In this paper we present the results confirmed that surface phases form the conductivity channel on the silicon surface which is an additional channel to the bulk one.

2 Experimental procedures

Experiments were carried out in an ultra-high vacuum (UHV) chamber (pressure 2×10^{-10} Torr). Si(100) wafers (*n*-type, 50 Ohm-cm) with a size of $19 \times 5 \times 0.45$ mm³ were cleaned *in situ* by the direct Joule heating up to 1200 °C for several minutes. The cleaned samples displayed the low energy electron diffraction (LEED) patterns typical for clean Si(100)2x1 surface.

The Au/Si(100) surface structures were prepared by Au deposition from an Au-coated tungsten filament at about 0.5 ML/min (1 monolayer (ML) equals 6.8×10^{14} at/cm² for Si(100), the evaporation rate site density for unreconstructed Si surface). Au atoms were deposited at room temperature (RT) and at 850 °C. Na was deposited from thermal getter cell (0.2 ML/min) onto the sample held at temperature 200 °C. The Na coverage was estimated assuming the saturation coverage of the Si(100)2x3-Na surface phase to be 1/3 ML [9]. In atoms were

deposited from Ta foil tube (1 ML/min). Deposition rates for Au and In were calibrated in accordance with phase diagrams [2].

For *in situ* surface conductivity measurements parallel to the silicon surface the DC four-point probe method was used. The measurements were carried out at RT in the range of current values from 0 to 100 μA with steps 5 μA . The ohmic conditions of the electrical contacts between the substrate and W electrodes, whose spacing was about 1.3 mm, were confirmed by the linear relation between voltage signal and electric of current. A sample was cooled down to RT during 1 h after fabrication to attain a stable conductance. Surface conductivity is defined as $\sigma \cdot d = G \cdot I/V \text{ Ohm}^{-1}$, where $G = 0.3101$ is dimensional coefficient [10] and d is the wafer thickness.

The measured surface conductivity σ has the two components: the conductivity through the bulk Si substrate σ_0 and that through the surface phase σ_{SP} , which is considered as extra-thin layer. If we propose that the Si(100)2x1 surface phase and as silicon-adsorbate surface phase are the conductivity channels through the surface, the conductivity of the clean silicon substrate in UHV is $\sigma = \sigma_0 + \sigma_{\text{Si(100)2x1}}$. To estimate the contribution of the silicon-adsorbate surface phase (Si(100)-A) we have to account for the Si(100)2x1 surface phase conductance:

$$\Delta\sigma = (\sigma_0 + \sigma_{\text{Si(100)-A}}) - (\sigma_0 + \sigma_{\text{Si(100)2x1}}) = \sigma_{\text{Si(100)-A}} - \sigma_{\text{Si(100)2x1}}.$$

3 Results and discussion

As we proposed, the formation of silicon-adsorbate surface phases results in appearance, of new conducting channels on the surface. Due to the shunting effect of the bulk substrate we measured the surface phase contribution into the bulk substrate conductivity. The changes of conductivity are to indicate an increal of conductivity if conductance of the silicon-adsorbate surface phase is greater than that of the Si(100)2x1 surface phase and a decrease of conductivity for a reversed relation between conductivities of these phases.

Fig. 1 shows the changes in conductivity and LEED patterns after Au adsorption at RT and annealing at 850 $^{\circ}\text{C}$ on Si(100) surface. At Au coverage from 0.1 to 0.5 ML c(8x2) superstructure is observed indicating formation of the Si(100)c(8x2)-Au surface phase. In the coverage range of 0.5-0.6 ML the 5x1 pattern appears, and when Au coverage is above 0.6 ML the Si(100) $\sqrt{2}$ 6x3-Au surface phase forms. The surface conductivity increases correlating with formation of new conductive channels on the surface. The conductivity increase is approximately proportional to gold atom concentration in Si-Au surface phase. It may be connected with an increase of charge carriers concentration in this surface phase when adsorbate coverage enhances.

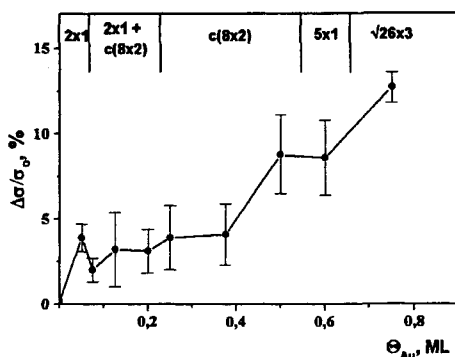


Figure 1. The surface conductivity and LEED changes for Au/Si(100) submonolayer system after formation of Si(100)-Au surface phases. The measurements were done at RT.

The difference in surface conductivity of the Si(100)2x3-Na surface phase $\Delta\sigma = -(1.5 \pm 0.6) \cdot 10^{-5} \text{ Ohm}^{-1}$ has an opposite sign in comparison with the Si(100)-Au surface phase. It means that the formation of the 2x3-Na surface phase (Na coverage is about 1/3 ML [9]) reduces surface conductivity. However, the exposure of a sample with the Si(100)2x3-Na surface phase in atomic hydrogen results in decreasing of conductivity, that can be associated with destruction of this surface phase (Fig. 2) as well as in the case with Si(100)2x1 surface.

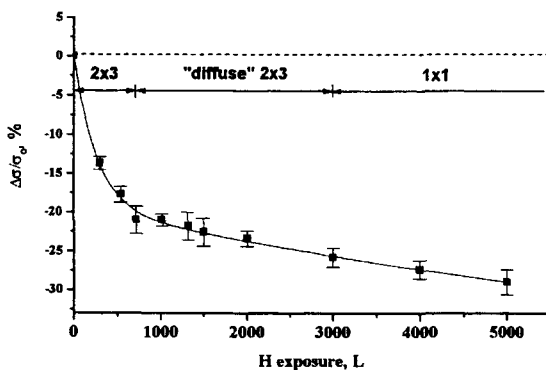


Figure 2. The surface conductivity and LEED changes after hydrogen exposure of the Si(100)2x3-Na surface phase at RT.

It indicates that the Si(100)2x3-Na surface phase forms the conductive channel despite the conductivity of the sample with this surface phase is less than that with the Si(100)2x1 surface phase.

Structural transformations of the surface during formation of Si(100)2x3-Na surface phase [11] also can play an important role in the reduction of conductivity. During formation of this phase a silicon surface with flat terraces converts to the surface which contains numerous small domains dividing by monoatomic steps [11]. The reduction of conductivity with the Si(100)2x3-Na surface phase can be associated with variation of surface roughness and numbers of the 2x3-Na domains [12].

Electrical measurements on the samples with the Si(100)4x3-In surface phase show that changes in conductivity in comparison with the surface phase of clean Si(100) is weak ($\Delta\sigma = (0.8 \pm 0.6) \cdot 10^{-5} \text{ Ohm}^{-1}$). The conductance of this surface phase is probably identical to the conductance of the Si(100)2x1 surface phase.

4 Conclusion

The electrical conductance of surface phases and extra thin layers of adsorbates on silicon surface was considered. We studied the influence of Si(100)2x1, Si(100)c(8x2)-Au, Si(100)5x1-Au, Si(100) $\sqrt{26}$ x3-Au, Si(100)2x3-Na, Si(100)4x3-In surface phases on electrical conductivity of the silicon substrate. It was shown that surface phases form the two-dimensional conductive channels on the surface. Their conductance may be greater or less than conductance then the one on the clean silicon surface Si(100)2x1 depending on the properties of surface silicon-adsorbate phases.

5 Acknowledgements

This research was made possible by financial support from Russian National Program "Surface Atomic Structures" (Grants No. 1.12.99), Russian Foundation for Fundamental Researches (Grant No. 99-02-16833), Russian-Ukrainian Scientific Program "Physics of Solid State Nanostructures" (Contract FTN-13(00)-P) and Russian Federal Program "Integratsia" (Project No. A0026).

References

1. Landau L. D., Lifshits E. M., *Statistical Physics* (Nauka, Moscow, 1964) (in Russian)
2. Lifshits V. G., Saranin A. A., Zotov A. V., *Surface Phases on Silicon* (Wiley, Chichester, 1994).
3. Bäuerle F., Mönch W., Henzler M., *J. Appl. Phys.* **43** (1972) 3917.

4. Hasegawa S., Tong X., Takeda S., Sato N., Nagao T., *Prog. Surf. Sci.* **60** (1999) 89.
5. Gasparov V. A., Grashulis V. A., Bondarev V. V., Bychkova T. M., Lifshits V. G., Churusov B. K., Galkin N. G., Plusnin N. I., *Vacuum* **41** (1990) 1207.
6. Lifshits V. G., Gavriluk Yu. L., Zotov A. V., Tsukanov D. A., *Phys. Low-Dim. Struct.* **1/2** (1997) 131.
7. Ryzhkov S. V., Tsukanov D. A., Lifshits V. G., *Phys. Low-Dim. Struct.* **7/8** (1998) 1.
8. Tsoukanov D. A., Ryzhkov S. V., Gruznev D. V., Lifshits V. G., *Appl. Surf. Sci.* **162-163** (2000) 168.
9. Glander G. S., Webb M. B., *Surf. Sci.* **224** (1989) 60.
10. Batavin V. V., Kontsevoy Yu. A., Fedorovitch Yu. V., *Izmerenie parametrov poluprovodnikovyh materialov i struktur* (Moscow, Radio i Svyaz, 1985) (in Russian).
11. Saranin A. A., Zotov A. V., Ryzhkov S. V., Tsukanov D. A., Lifshits V. G., Ryu J.-T., Kubo O., Tani H., Harada T., Katayama M., Oura K., *Phys. Rev. B* **58** (1998) 4972.
12. Ryjkov S. V., Nagao T., Lifshits V. G., Hasegawa S. (to be published)

MORPHOLOGY AND OPTICAL PROPERTIES OF Si(111)/CrSi₂/Si AND Si(111)/Mg₂Si/Si SYSTEMS WITH SELF-ORGANIZED QUANTUM DOTS

N. G. GALKIN, A. M. MASLOV, S. I. KOSIKOV

*Institute for Automation and Control Processes, Far Eastern Department of RAS
Radio 5, 69004 Vladivostok, Russia*

A. O. TALANOV, K. N. GALKIN

*Institute of Physics and Information Technologies of Far Eastern State University
Sukhanova 8, 690090 Vladivostok, Russia*

E-mail: galkin@iacp.vl.ru

Growth conditions of CrSi₂ and Mg₂Si quantum dots, their sizes and density on Si(111) substrates and optical properties of new materials were investigated. Technologies of CrSi₂ and Mg₂Si island formation on Si(111) were proposed. Two direct interband transitions at 0.95 eV and 1.30 eV were observed in CrSi₂ quantum dot materials. It was shown that Mg₂Si quantum dots do not influence strongly optical properties of silicon substrate.

1 Introduction

The systems with semiconductor quantum dots attract significant attention of researchers due to a wide range of new physical phenomena caused by 3D confinement of charge carriers. Self-organized epitaxial nanostructures are considered nowadays as one of the most acceptable systems for *in situ* formation of quantum dots without photolithography and etching processes. Semiconductor metal silicides (CrSi₂, β -FeSi₂, Mg₂Si) are successfully used for epitaxial growth of continuous films, however, study of self-organizing silicide quantum dots (QDs) on silicon (CoSi₂ [1]) only begins.

In this paper we present morphology and optical properties of new materials with buried CrSi₂ and Mg₂Si quantum dots grown on silicon substrates.

2 Experimental details

The ultrahigh vacuum UHV VARIAN system with a base pressure 2×10^{-10} Torr equipped with AES-EELS optics, four sublimation sources (Si, Cr, Fe, Mg), a manipulator, a holder for three samples and a quartz thickness sensor. It was possible to anneal separately each sample with direct current. Silicon p-type, 10 Ω ·cm, (111) wafers were used as substrates. The native oxide and residual carbon contaminants were removed in the UHV chamber by annealing at 1250 °C

for 120-180 s. Metal deposition rates were 0.001-0.002 nm/s. Silicon deposition rate was 0.016 nm/s.

Quantum dots of A-type (CrSi_2) were formed by chromium deposition (0.1-1.0 nm) on a hot substrate at 500 °C. Mg_2Si quantum dots were formed in two stages. At the first stage an amorphous silicon layer (1.0 nm) was deposited at room temperature on Si(111)7x7 surface. At the second one the magnesium layer (0.6-1.2 nm) was deposited onto amorphous silicon at room temperature and then the sample was annealed at 240-370 °C. Silicon layers (3 nm) were grown by solid phase epitaxy at 350-400 °C atop of each layer of the silicide quantum dots. AES and EELS spectra were recorded on each stage of the quantum dot formation.

Morphology of the samples with buried QDs was investigated with an atomic force microscope Solver P47 [2] and Raman spectroscopy. Optical transmittance (T) and reflection (R) spectra were registered in the energy range 0.1-6.2 eV. Calculations of optical functions have been carried out with the RT-procedure and the Kramers-Kronig integral relations.

3 Results and discussion

Two peaks were only observed at 520 cm^{-1} and 300 cm^{-1} from Raman spectra of Si(111)/ CrSi_2 /Si system. The 520 cm^{-1} peak concerns the first order from monocrystalline silicon. As there is no displacement of this peak we conclude that the silicon, which was atop of a layer of quantum dots, to be epitaxial one. The 300 cm^{-1} weak peak relates to the first order signal from bulk CrSi_2 (310 cm^{-1} [3]). The small observable shift of this peak can testify for the benefit of small islands with a strained crystal lattice. It is confirmed by the AFM images of the samples with CrSi_2 QDs (Fig. 1.) Island density increases from 5×10^{11} to $1 \times 10^{12}\text{ cm}^{-2}$ with

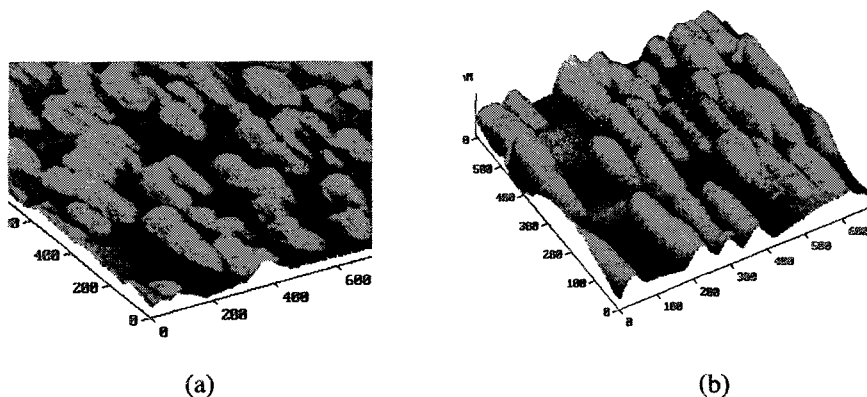


Figure 1. AFM images of Si(111) CrSi_2 /Si samples for deposited Cr 0.3 nm (a) and 1.0 nm (b).

the increase of the thickness of deposited Cr from 0.3 to 1.0 nm. Nevertheless, the island size remains approximately identical (width 50-80 nm, length 100-200 nm, height 10-15 nm). According to AES and EELS measurements CrSi_2 islands are under a layer of silicon and have identical orientation. They look to grow simultaneously when 1 nm Cr was deposited.

Optical analysis of the samples with QDs show that their T-spectra are comparable to T-spectrum of bare silicon. Contribution of the layer containing CrSi_2 QDs to the absorption coefficient is observed at 1.0-2.5 eV. Two direct interband transitions at 0.95 eV and 1.30 eV were extracted (Fig. 2). As the direct

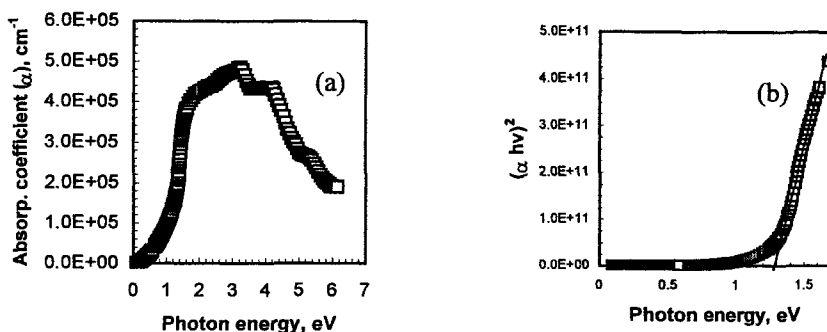


Figure 2. Absorption spectra (a) and square of product of the absorption coefficient (α) and photon energy versus photon energy (b) for Si(111)/QD CrSi_2 /Si structure fabricated with 0.5 nm deposited Cr.

interband transitions are realized, one can also expect the light emission from Si(111)/QD CrSi_2 /Si structures in this energy range.

Formation of Mg_2Si QDs was controlled with AES and EELS analysis. In Raman spectra a strong peak at 520 cm^{-1} and very weak broad peak around 290 cm^{-1} were only observed. So, the contribution of Mg_2Si phase is very small, but the top silicon layer is epitaxial one. AFM images showed that annealing of the Si(111)/a-Si/Mg system at 240°C provides formation of islands with a lateral size of 40-80 nm and height of 6-8 nm. Falls at the foots of these islands indicate that formation of Mg_2Si is connected with transport of silicon atoms from the island foot to its top. Flat spots on the silicon substrate show that the silicide formation is accompanied with evaporation of magnesium from the silicon surface (magnesium is known to evaporate intensively from a silicon surface at temperatures higher than 220°C [4]). The density of Mg_2Si islands did not exceed $4 \times 10^9 \text{ cm}^{-2}$. Transmittance and reflectance spectra of the samples with Mg_2Si QDs had only minor modifications in UV-VIS region, in contrast to those for CrSi_2 QDs. We think that it is connected with the small size and small surface density of Mg_2Si QDs. An increase of their density up to 5×10^{11} – $1 \times 10^{12} \text{ cm}^{-2}$ is desired. The structure with relatively thick protective layer of silicon, like Si(111)/a-Si/Mg (0.6-1.0 nm) /a-Si (3.0 nm), looks favourable to achieve that.

4 Conclusions

The growth conditions of CrSi_2 and Mg_2Si quantum dots on $\text{Si}(111)7\times7$, their sizes and surface density and optical properties were investigated. It was shown that Cr deposition (0.3-1.0 nm) onto hot Si substrate results in the formation of CrSi_2 islands with high density ($5\times10^{11} - 1\times10^{12} \text{ cm}^{-2}$). Two-stage technology for fabrication of Mg_2Si quantum dots on $\text{Si}(111)$ was proposed, but quantum dot density did not exceed $4\times10^9 \text{ cm}^{-2}$. Two direct interband transitions at 0.95 eV and 1.30 eV were observed in CrSi_2 quantum dot structures, while Mg_2Si quantum dots did not influence strongly optical properties of the silicon substrate.

5 Acknowledgements

We thank Prof. B. N. Mavrin and his collaborators in Institute of Spectroscopy RAS (Troitsk, Russia) for the Raman spectroscopy experiments. This work was performed with financial support from the Russian Foundation of Fundamental Researches (Grant No. 00-02-81000) and the Russian Ministry of Professional Education "Fundamental Researches in the Fields of Electronics and Radioengineering".

References

1. Goldfarb I., Briggs G. A. D., *Phys. Rev. B* **60** (1999) 4800.
2. <http://www.ntmdt.ru>
3. Lange H., Giehler M., Henrion W., Fenske F., Sieber I., Oertel G., *Phys. Stat. Sol. (b)* **171** (1992) 63.
4. Mahan J. E., Vantomme A., Lagouche G., Becker J. P., *Phys. Rev. B* **54** (1996) 16695.

MICROCAVITY ENHANCEMENT OF SECOND-HARMONIC GENERATION AND RAMAN SCATTERING IN PHOTONIC CRYSTALS OF POROUS SILICON

**M. G. MARTEMYANOV, T. V. DOLGOVA, A. I. MAYDIKOVSKII,
A. A. FEDYANIN, O. A. AKTSIPETROV**

*Department of Physics, Moscow State University
119899 Moscow, Russia*

D. SCHUHMACHER, G. MAROWSKY

*Laser-Laboratorium Goettingen
Hans-Adolf-Krebs-Weg 1, D-37077 Goettingen, Germany*

V. A. YAKOVLEV

*Institute of Spectroscopy, Russian Academy of Sciences
142092 Troitsk, Moscow reg., Russia*

G. MATTEI

*Istituto di Metodologie Avanzate Inorganiche, CNR
Area della Ricerca di Roma, C.P. 10, Monterotondo Scalo, 00016, Italy*

E-mail: misha@astral.ilc.msu.su

Localization of light in the vicinity of a microcavity layer incorporated in a photonic crystal of porous silicon leads to 150-fold enhancement of the second - harmonic intensity and 30-fold enhancement of Raman scattering around the microcavity mode.

1 Introduction

Recently, photonic crystals (PCs) and microcavities (MCs) have attracted a great deal of attention for both fundamental and applied research. In such microstructures electromagnetic field propagation is forbidden for a range of frequencies called photonic band gap, in analogy to semiconductor band gap [1]. This phenomenon based on destructive interference of forward- and backward-propagating electromagnetic fields leads to the variety of new optical effects. Large optical dispersion near the band edges [2], optical bistability and the enhancement of the nonlinear-optical response at the edges of photonic band gap due to the fulfillment of phase-matching conditions are observed in PCs [3]. In a microcavity the active layer is surrounded by PCs acting as distributed cavity mirrors. Varying the parameters of PC mirrors allows to control the quality of MCs and manage

localization of light in the MC active layer. The increased optical field could serve as a source of enhanced nonlinear-response of MCs.

In this paper, the second-harmonic (SH) intensity spectroscopy is proposed as a direct probe of localization of light inside porous silicon PCs and MCs with the cavity mode located inside the photonic band gap. The choice of microstructures based on porous silicon is attributed to their great practical importance since the all-silicon electrochemical technique of the growth of such structures could be easily incorporated in the silicon technology. The enhancement effects of SH generation and Raman scattering in such microstructures in the vicinity of the MC mode are studied.

2 Samples and setup

The MC samples were fabricated by the standard procedure of electrochemical etching of Si(001) wafers of resistivity $0.01 \Omega\text{-cm}$ with periodical modulation of the current flowing through the wafer perpendicular to its surface. This leads to the growth of porous silicon layers with different porosity, and therefore, with varying dielectric constant. The studied MC sample (Fig. 1) consisted of approximately 400 nm thick MC active layer with high porosity (~ 0.88) surrounded with two PCs fabricated from 5 pairs of 200 nm-thick (porosity ~ 0.88) and 160 nm thick (porosity ~ 0.8) layers each. The parameters of MCs were checked by force scanning microscope working in the shear-force mode.

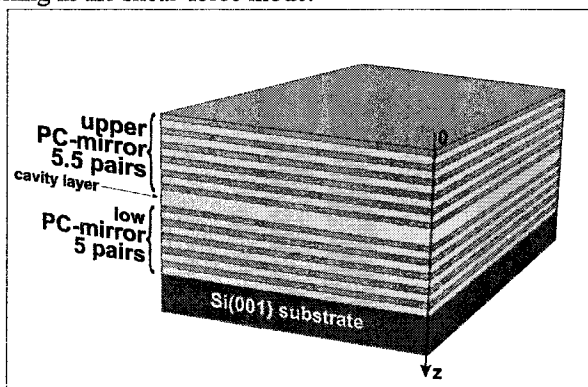


Figure 1. The schematic diagram of the porous silicon microcavity.

The s-polarized output of a tunable nanosecond parametric generator/amplifier laser system operating in the interval of 730–1000 nm was used as a fundamental radiation for SH spectroscopy. The SH light was selected by appropriate filters and detected by a photomultiplier. For Raman measurements we have employed an s-polarized Ar^+ ion laser beam at 514.5 nm focused in a spot of 150–200 μm onto the sample with a power 7 mW to avoid a PS structure damage. Raman spectra were

recorded by Spex Triplemate spectrograph equipped with a charge coupled device detector. From the obtained spectra we have calculated the integrated intensity of the silicon band at 520 cm^{-1} .

3 Experimental

Upper panel of Fig. 2 shows the spectrum of SH intensity for porous silicon MC in

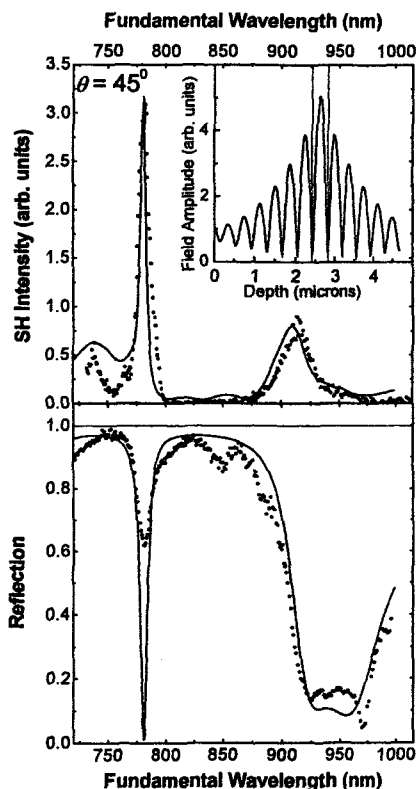


Figure 2. Upper panel: SH intensity spectrum measured in porous silicon microcavity in s-in, p-out geometry. Lower panel: the spectrum of linear reflection of s-polarized fundamental radiation. The inset: the calculated spatial distribution of the fundamental field amplitude inside the microcavity. Lines indicate the boundaries of the microcavity active layer.

s-in, p-out polarization combination for 45 degrees angle of incidence. For comparison the spectrum of the linear reflection of s-polarized radiation is depicted in the lower panel. In the vicinity of the microcavity mode, which is located for this angle of incidence at 780 nm, the SH intensity is more than 150 times enhanced.

Inset in Fig. 2 shows the calculated spatial distribution of the fundamental radiation amplitude which is a superposition of forward- and backward-propagating components of the fundamental field using the matrix method. The fundamental radiation is strongly localized in the vicinity of the MC active layer enhancing the nonlinear response.

We have measured an enhancement factor of Raman signal of Si 510 cm^{-1} band larger than 30 for such structure [4]. The enhancement obtained can be associated with the coupling of both laser radiation and Stokes photons of porous silicon with the microcavity mode at the optimal laser beam incidence and scattering angles.

4 Acknowledgements

This work was supported by the Russian Foundation for Basic Research (RFBR) and Deutsche Forschungsgemeinschaft (DFG): RFBR grant 00-02-04026, DFG grants 436 RUS 113/439/0 and MA 610/20-1, RFBR grant 00-02-16253, special RFBR grant for Leading Russian Science Schools 00-15-96555; NATO Grant PST.CLG975264, Russian Federal Program "Center of Fundamental Optics and Spectroscopy", and Program of Russian Ministry of Science and Technology "Physics of Solid State Nanostructures".

References

1. Yablonovitch E., Inhibited spontaneous emission in solid-state physics and electronics, *Phys. Rev. Lett.* **58** (1987) pp. 2059-2062.
2. Imhof A., Vos W. L., Sprik R., Lagendijk A., Large dispersive effects near band-edges of photonic crystals, *Phys. Rev. Lett.* **83** (1999) pp. 2942-2945.
3. Nakagawa S., Yamada N., Mikoshiba N., Mars D. E. Second-harmonic generation from GaAs/AlAs vertical cavity, *Appl. Phys. Lett.* **66** (1995) pp. 2159-2162.
4. Kuzik L. A., Yakovlev V. A., Mattei G., Raman scattering enhancement in porous silicon microcavity, *Appl. Phys. Lett.* **75** (1999) pp. 1830-1832.

STRUCTURAL AND ELECTRICAL CHARACTERIZATION OF THIN CRYSTALLINE CaF_2 LAYERS GROWN BY MBE ON $\text{Si}(111)$

G. GUIRLÉO, F. BASSANI

*Centre de Recherche sur les Mécanismes de la Croissance Cristalline, CNRS
Campus de Luminy: Case 913, 13288 Marseille cedex 9, France*

E-mail: guirleo@crmc2.univ-mrs.fr

The surface morphology and current-voltage characteristics of 3 nm thick CaF_2 layers are presented. The layers have been grown by molecular beam epitaxy on a 50 nm thick Si buffer at different substrate temperatures. Those deposited at low and high temperatures have very good insulating properties with electrical breakdown fields of about 10^7 V/cm.

1 Introduction

Silicon MOS technology is currently the most developed and well established one for microelectronic device production. The insulating material used within this technology is silicon dioxide (SiO_2). However, because of an amorphous nature it is not suitable for heteroepitaxial growth on Si substrates. This shortcoming limits seriously the fabrication of Si based quantum effect devices like resonant tunneling diodes, lasers, etc. [1]. From this point of view, calcium fluoride (CaF_2), which has just 0.6 % lattice mismatch with $\text{Si}(111)$, may advance greatly developments in Si-based nanodevices. The main requirements in this case are good structure morphology of CaF_2 layers and their sufficient electrical stability as well.

In this work we have attempted to find MBE growth conditions that allows epitaxial elaborating nanometer thick CaF_2 layers on $\text{Si}(111)$ substrates with high quality electrical properties. The results on electrical resistance are presented and compared to the data available for Si/CaF_2 and Si/SiO_2 systems.

2 Experimental procedure

The experimental setup consists of an ultrahigh vacuum (UHV) *RIBER* system [2]. A base pressure in the 10^{-11} Torr range is obtained by ion-pumping. In the growth chamber, Si is evaporated by means of an electron gun evaporator. CaF_2 was congruently evaporated from a standard, temperature controlled, diffusion cell with a pyrolytic boron nitride crucible. The deposition rates of both Si and CaF_2 have been calibrated by weight measurements. Si and CaF_2 deposition rates are 0.56 Å/s and 0.35 Å/s, respectively.

Prior to UHV loading, the 2'' Si(111) substrates (n-type) are chemically cleaned according to the Shiraki cleaning procedure. The last stage consists of a deep in a $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solution, producing a thin silicon oxide film, subsequently followed by a deep in a diluted HF solution to obtain a hydrogenated surface.

Beforehand CaF_2 deposition (3 nm), a Si buffer (50 nm) is grown, at 750 °C, on a clean Si(111) surface. Crystallinity and surface morphologies of these layers are assessed by reflection high energy diffraction and atomic force microscopy (AFM). The CaF_2 deposition is done using three different growth regimes: in sample A the CaF_2 layer has been deposited at room temperature, in sample B a ramp from 300 to 700 °C has been used and sample C is fabricated at 700 °C. It has been previously shown that CaF_2 layers grown at low substrate temperatures ($T_s < 400$ °C) exhibits A-type epitaxy while those grown at high temperatures are characterized by B-type epitaxy [3]. For direct imaging of the CaF_2 layer surface a contact mode AFM in air has been used.

Metal-insulator-semiconductor devices have been made from CaF_2/Si samples and investigated by current-voltage (I - V) measurements using a Hewlett Packard 4140B pA meter. Aluminum is deposited through a metallic mask with circular holes of 800 μm in diameter. A schematic cross section of the device is shown in Fig. 1.

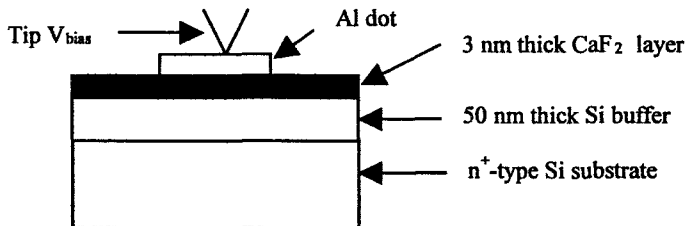


Figure 1. A schematic cross-section of the device fabricated to investigate electrical properties of CaF_2 layers.

3 Results and discussion

AFM images recoded for the samples studied are show in Fig. 2. Samples A and C present smooth terraces with a step height of one molecular CaF_2 layer. In addition, 2D triangular CaF_2 islands nucleated on the terraces are observed. More details concerning the growth modes of CaF_2 on the Si buffer is described elsewhere [4]. While samples A and C exhibit a flat surface morphology, sample B presents some holes with a triangular shape. The depth of these holes is roughly equal to the total thickness of the CaF_2 layer. The formation of these holes results from the coalescence of 3D CaF_2 islands. These triangular pits have been previously observed by Sokolov et al. and are supposed to have only one monolayer at the bottom [5].

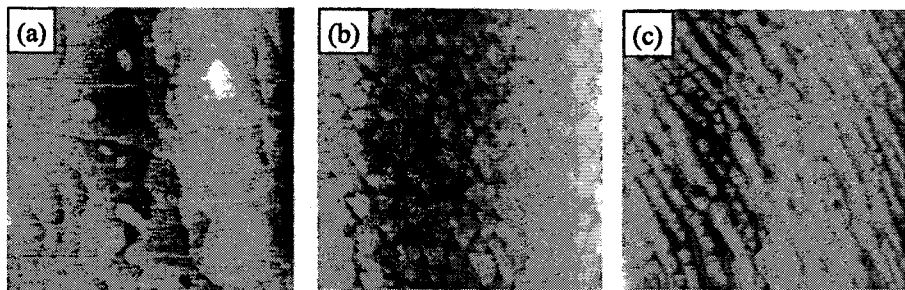


Figure 2. AFM images from the three samples: sample A (a), sample B (b), and sample C (c). The scan size is $4 \times 4 \mu\text{m}^2$.

Fig. 3 displays the room temperature I - V characteristics for the samples grown at low and high temperatures (samples A and C). It is worthwhile to notice that sample B exhibits much higher currents for the same voltage. For instance, a current density of the order of 10^{-1} A/cm^2 at 1 V is measured for sample B while for samples A and C it is in the range of $10^{-11} - 10^{-10} \text{ A/cm}^2$. This behavior is attributed to the presence of pits which short circuit the CaF_2 layer between two electrodes resulting in high conductive paths. On the contrary, the current through samples A and C is very low implementing good insulating properties of such thin CaF_2 layers.

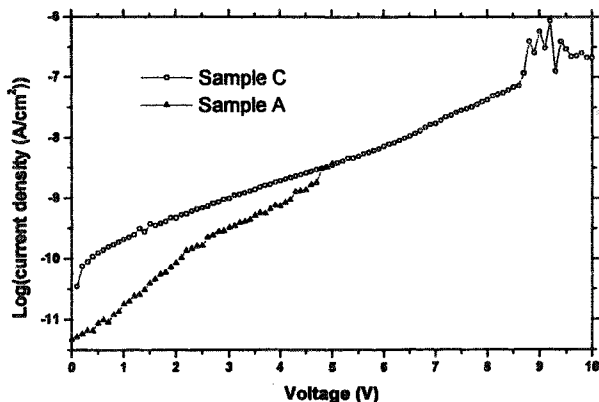


Figure 3. Room temperature I - V characteristics for samples A and C. The Al dot area is $5.03 \times 10^{-3} \text{ cm}^2$.

Note that the current density of sample A is smaller than that of sample C for a bias lower than 4.7 V. In addition, the I - V characteristics of both samples can be fitted by an exponent in the form

$$I = I_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right], \quad (1)$$

where n is the ideality factor. The ideality factors extracted from equation (1) are about 25 and 44 for samples A and C, respectively. Such high values suggest that

most of the applied voltage drops in the CaF_2 layer. Further I - V measurements at different temperatures are in progress to elucidate the mechanisms that govern the transport in such thin CaF_2 films.

For voltage polarities higher than 8.7 V, the current undergoes to a very strong increase: the structure is modified becoming leaky. One may estimate the electrical breakdown field to be 1.48×10^7 V/cm. This value can be compared to that found by Cho et al. (1.4×10^6 V/cm) for a 100 nm thick CaF_2 layer [3] and to that found by Harari et al. (2.8×10^7 V/cm) for a 4 nm thick SiO_2 layer [6].

4 Conclusions

We have presented surface morphologies and current-voltage characteristics of ultrathin (3 nm) CaF_2 layers grown at different substrate temperatures on a 50 nm thick Si buffer. When the CaF_2 is deposited at room temperature or at high temperature (around 700 °C), the layers obtained exhibit atomically flat surfaces, as well as very good insulating properties. An electrical breakdown field has been measured to be about 10^7 V/cm which is one of the best values ever reported for the Si/ CaF_2 system.

5 Acknowledgements

We would like to thank A. Kholod and M. Liniger for the help in electrical measurements and discussions of the results obtained.

References

1. Sinharoy S., *Thin Solid Films* **187** (1990) 231.
2. Bassani F., Vervoort L., Mihalcescu I., Vial J. C., d'Avityaya F. Arnaud, *J. Appl. Phys.* **79** (1996) 4066.
3. Cho C.-C., Liu H. Y., Gnade B. E., Kim T. S., *J. Vac. Sci. Technol. A* **10** (1992) 769.
4. Bassani F., Guirleo G., F. Arnaud d'Avitaya, submitted to *J. Crystal Growth*.
5. Sokolov N. S., Alvarez J. C., Gastev S. V., Shusterman Yu. V., Takahashi I., Itoh Y., Harada J., Overney R. M., *J. Crystal Growth* **169** (1996) 40.
6. Harari E., *J. Appl. Phys.* **49** (1978) 2478.

SWITCHING EFFECT IN LEAD PHTHALOCYANINE NANOSTRUCTURE

N. A. POKLONSKI, E. F. KISLYAKOV, G. G. FEDORUK, D. I. SAGAIK, A. I. SIAGLO, S. A. VYRKO

Belarusian State University, 220050 Minsk, Belarus

E-mail: poklonski@phys.bsu.unibel.by

Electronic structure model of the lead phthalocyanine (PbPc) stacking-fault nanostructure is proposed. Semi-empirical molecular orbital calculations show $0.6e$ charge transfer from the lead atom to the macrocyclic ring of the PbPc molecule. Stack of PbPc molecules is considered as a metal-filled nanotube. This allows for the first time quantitative interpretation of the earlier observed switching effect in the PbPc films. 1D quantum transport in the nanostructure is discussed and charge carrier (polaron) effective mass is estimated.

Phthalocyanine nanostructures in thin solid films are interesting model objects for charge transport study in low dimensional quantum systems [1]. In particular, stacks of such molecules [2] are quasi one-dimensional quantum wires. A theory of charge transport in such systems is very important for nowadays science [3].

Lead phthalocyanine (PbPc) is known as one of the first discovered organic metal [4,5]. In polycrystalline PbPc films ($\approx 0.6 \mu\text{m}$ thickness) electrical switching effect (eight orders conduction jump at critical field $\approx 4 \cdot 10^4 \text{ V/cm}$) has been observed [6,7]. This phenomenon has no quantitative interpretation till now. The purpose of this work is theoretical investigation of charge transport in PbPc and, in particular, switching effect interpretation.

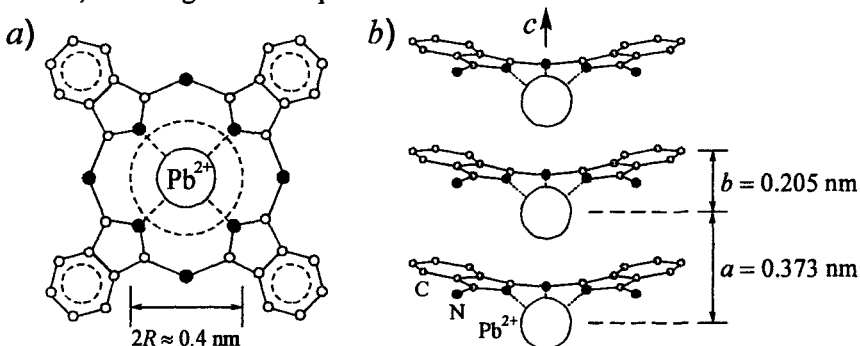


Figure 1. Lead phthalocyanine molecule (a); a nanostructure consisting of PbPc molecules (b); $2R$ is the diameter of conducting channel. Hydrogen atoms are not shown.

Contrary to other phthalocyanines, PbPc molecules (Fig. 1(a)) are not flat. They have characteristic shuttlecock form and can crystallize in monoclinic phase

[4]. In the crystal of PbPc, the molecules are stacked linearly in the direction of the c -axis parallel to the fourfold axis of the molecule as shown in Fig. 1(b). The interatomic distance between lead atoms within a molecular column (0.373 nm) is slightly larger than that in lead metal (0.348 nm). This intermolecular arrangement in a column and the observed [5] temperature dependence of electrical conduction in the direction of the c -axis suggest that PbPc is one-dimensional conductor.

We have carried out semi-empirical molecular orbital calculations of PbPc molecule employing MOPAC 7.0 program with the PM3 parameterization [8]. The calculations give ≈ 2 eV for the height of the potential barrier for Pb^{2+} ion tunneling through the macrocyclic ring. Our calculations show $0.6e$ (where e is the electron charge) charge transfer from the Pb atom to the macrocyclic ring. Thus, the column of PbPc molecules is analogous to the metal-filled nanotube [9] with the 0.2 nm radius of conducting channel. As in [9], we assume, that positive charge inside nanotube is homogeneously distributed. The linear charge density of the negative charge on its surface is: $\chi = 0.6e/a < 0$, where $a = 0.373$ nm is spatial period of one-dimensional infinitely long nanotube (we also assume, that the surface distribution of the negative charge is homogeneous). For such spatial charge distribution, the electrostatic potential has the form [10]:

$$\phi(r) = -\frac{\chi}{4\pi\epsilon_0} \left(\frac{r^2}{R^2} - 1 \right), \quad (1)$$

where ϵ_0 is the electrical constant, R is the nanotube radius. From (1) we get $\phi(r=0) = -0.6e/4\pi\epsilon_0 a = 2.32$ V. As a whole nanotube is electrically neutral, therefore $\phi(r \geq R) = 0$.

The calculations, similar to those in [9], show that in the PbPc column there is only one transverse energy level (single subband of motion perpendicular to the column axis). Therefore, it looks as a true one-dimensional system.

We shall consider single stack of PbPc molecules between two identical electrodes (Fig. 2) in situation, when electrode-nanotube contact resistance is negligibly small. The resistance of nanostructure is entirely determined by the stacking-fault (Fig. 2(a)) and according to the Landauer formula [11] in $T \rightarrow 0$ limit conductance of the nanotube is:

$$G = \frac{2e^2}{h} D(E_F) = \frac{D(E_F)}{12.9 \text{ k}\Omega}, \quad (2)$$

where $D(E_F)$ is the transmission function from one contact to another for the electron with the kinetic energy equal to Fermi energy E_F . When the stacking-fault is absent (Fig. 2(b)), then $D(E) \equiv 1$.

We approximate the stacking-fault by the rectangular potential barrier. According to Fig. 1(b) and Fig. 2(a) the barrier width is $d = a + 2b - 2r_l = 0.53$ nm, where $r_l = 0.126$ nm is the Pb^{2+} ion radius from [12].

Since there are no electrons in the middle of stacking-fault under the

equilibrium (no current), electrostatic potential here is equal to zero. So, the potential energy $U(z)$ of the electron along the nanotube axis is $e\varphi_0 = e\varphi(r=0) = -2.32$ eV far away from the stacking-fault and equal to zero inside it (Fig. 2). The height of the potential barrier is $U_0 = |e\varphi_0|$. Thus, according to [13]:

$$D(E) = \frac{4k^2\alpha^2}{(k^2 + \alpha^2)^2 \operatorname{sh}^2(\alpha d) + 4k^2\alpha^2}, \quad (3)$$

where $k = \hbar^{-1}\sqrt{2mE}$, $\alpha = \hbar^{-1}\sqrt{2m(U_0 - E)}$.

The Fermi energy of the one-dimensional electron system with one subband of transverse motion at $T = 0$ K is [14]:

$$E_F = \frac{\pi^2 \hbar^2 n^2}{8m}, \quad (4)$$

where n is the linear density of conduction electrons, m is the effective mass for the longitudinal motion of the conduction electron inside nanotube, $\hbar = h/2\pi$ is Planck constant.

There are four valence electrons in Pb atom. Two of them are in the completely filled first Brillouin zone (see, for example, [14]) and 1.4 electrons per Pb atom are in the second Brillouin zone. Therefore, $n = 1.4/a$. If $m > 0.6 m_0$, where m_0 is the free electron rest-mass, then $E_F < U_0$.

The only free parameter in our model is the effective mass of conduction electron. If $m = 5.7 m_0$, according to (3)–(4), $D(E_F)$ changes from 10^{-8} to 1, when the PbPc nanostructure goes from the “off-state” (Fig. 2(a)) to the “on-state” (Fig. 2(b)). This can explain the conduction jump observed in [6]. The total conductance is the sum of conductances of many nanostructures.

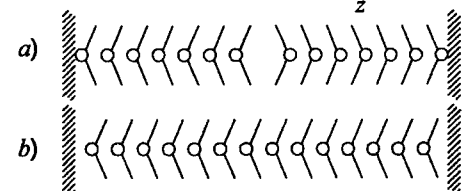


Figure 2. Column of PbPc molecules, placed between two identical metallic electrodes: *a*) with stacking-fault (“off-state”); *b*) without defect (“on-state”); $U(z)$ is the potential energy of conduction electron.

They have minimum resistance among all other possible molecular configurations the film. The observed value of critical field ($\approx 4 \cdot 10^4$ V/cm) [6] is in accordance with the potential barrier height for Pb^{2+} ion tunneling through the macrocyclic ring calculated by us. STM data [15] also agree with the calculated height value. All these facts give the strong support for our interpretation of the switching effect in PbPc films. Since $E_F = 232$ meV (ten times

larger than the kinetic energy of electron at 300 K), the room temperature measurements [6,7] do not differ essentially from calculations with (2).

In conclusion, our interpretation of the switching effect in PbPc films gives the opportunity to estimate the charge carrier effective mass in the PbPc molecular column. The relatively large effective mass value estimated here suggests that the charge carrier is polaron. Polaronic transport in organic matter is commonly accepted and widely discussed in literature [16].

References

1. Fischer C. M., Burghard M., Roth S., von Klitzing K., *Europhys. Lett.* **28** (1994) 129.
2. Zlatkin A., Yudin S., Simon J., Hanack M., Lehman H., *Adv. Mater. Opt. Electron.* **5** (1995) 259.
3. Londergan J. T., Carini J. P., Murdock D. P., *Binding and scattering in two-dimensional systems: applications to quantum wires, waveguides and photonic crystals* (Springer-Verlag, Berlin, 1999).
4. Ukei K., *Acta Cryst. B* **29** (1973) 2290.
5. Ukei K., Takamoto K., Kanda E., *Phys. Lett. A* **45** (1973) 345.
6. Hamann C., Höhne H. - J., Kersten F., Müller M., Przyborowski F., Starke M., *Phys. Stat. Sol. (b)* **50** (1978) K189.
7. Frauenheim Th., Hamann C., Müller M., *Phys. Stat. Sol. (a)* **86** (1984) 735.
8. Stewart J. J. P., *J. Comp. Chem.* **10** (1989) 209.
9. Poklonski N. A., Kislyakov E. F., Fedoruk G. G., Vyrko S. A., *Phys. Solid State* **42** (2000) 1666.
10. Batygin V. V., Toptygin I. N., *Sbornik zadach po elektrodinamike* (Nauka, Moscow, 1970) (in Russian).
11. Landauer R., *IBM J. Res. Develop.* **32** (1988) 306.
12. *Fizicheskie velichiny: Spravochnik*, ed. by Grigor'ev I. S., Meilikhova E. Z. (Energoatomizdat, Moscow, 1991) (in Russian).
13. Landau L. D., Lifshits E. M., *Quantum Mechanics*, 3rd ed. (Pergamon, Oxford, 1977).
14. Kagoshima S., Nagasawa H., Sambongi T., *One-Dimensional Conductors* (Springer-Verlag, Berlin, 1988).
15. Strohmaier R., Ludwig C., Petersen J., Gompf B., Eisenmenger W., *J. Vac. Sci. Technol. B* **14** (1996) 1079.
16. Movaghar B., *J. Molec. Electronics* **3** (1987) 183; *ibid.* **4** (1988) 79.

PHOTOREFLECTANCE DIAGNOSTICS OF NANOMETER DIELECTRIC FILMS

P. ADAMSON

*Institute of Physics, University of Tartu
51014 Tartu, Estonia*

E-mail: peep@fi.tartu.ee

The effect of nanometer dielectric films on the reflection of linearly polarized light from transparent or absorbing bulk substrate is investigated. Approximate formulas describing the contribution of such layers to Fresnel reflectivity for s- and p-polarized light are obtained. It is shown that approximate expressions describing the differential reflectivity can be used for unambiguous determination of the thickness and refractive index of nanometer-scale films.

1 Introduction

The fast development of nanotechnology in recent years posed a problem of optical diagnostics of nanometer-scale structures. The photoreflectance methods (in the case of ultrathin films the differential reflection methods [1,2] which are based on the direct measurement of the contribution of an ultrathin layer to the reflectivity) have been successfully employed for investigation of ultrathin layers because they have the advantage of simplicity of experimental setup [3,4]. The theoretical basis of photoreflectance methods is the conventional electromagnetic theory of plane wave reflection from a layered medium. From an analytical standpoint the nanometer-scale layers have an important merit: the thickness is much less than an optical wavelength which will allow to analyze the reflection problem within the framework of perturbation theory.

The purpose of this paper is to show how one can use the differential reflectivity of linearly polarized light to determine parameters of nanometer dielectric films on bulk transparent or absorbing substrates. Relatively simple approximate expressions for the reflectivity of s- and p-polarized light are derived. On the basis of these expressions, a number of novel ways to determine optical parameters of the nanometer-scale layers are shown through the differential reflectivity.

2 Transparent substrate

We shall consider the reflection of s- and p-polarized plane wave with vacuum wavelength λ in a medium a with permittivity $\varepsilon_a = n_a^2$ from a plane-parallel layer

medium consisting of a semi-infinite substrate s with the permittivity $\varepsilon_s = n_s^2$ and two layers with the effective thicknesses d_1 and d_2 and the local effective permittivities ε_1 and ε_2 . We assume that all the media are isotropic, entirely transparent and the magnetic permeabilities are equal to 1. We analyze the situation where the angle of incidence φ_a differs slightly from the Brewster angle $\varphi_B = \arctan(n_s/n_a)$ for the substrate, so that the condition $\Delta\varphi/\varphi_B \ll 1$ is satisfied, where $\Delta\varphi = |\varphi_a - \varphi_B|$. Let the substrate initially have only one layer with the parameters ε_1 and d_1 . We then calculate $((R_2 - R_1)/R_1)^{(p)} \equiv (\Delta R/R_1)^{(p)}$, which is the relative change in the reflection coefficient, occurring when a second surface layer with the parameters ε_2 and d_2 is applied to the first layer. In the second order with respect to the small parameters we obtain:

$$\left(\frac{\Delta R}{R_1}\right)^{(p)} = \frac{(R_0^{(p)} + \Delta R_2^{(p)}) - (R_0^{(p)} + \Delta R_1^{(p)})}{(R_0^{(p)} + \Delta R_1^{(p)})} \approx \left(\frac{\Delta R}{R_1}\right)_B^{(p)} \frac{\delta_B^2}{((\varphi_a - \varphi_B)^2 + \delta_B^2)}, \quad (1)$$

where

$$\delta_B = \frac{2\pi d_1 n_a n_s \varepsilon_s}{\lambda \varepsilon_1 (\varepsilon_a + \varepsilon_s)^{1/2}} \left| \frac{(\varepsilon_1 - \varepsilon_a)(\varepsilon_1 - \varepsilon_s)}{(\varepsilon_s^2 - \varepsilon_a^2)} \right|, \quad (2)$$

and $(\Delta R/R_1)_B^{(p)}$ is the relative change in the reflection coefficient at precisely the Brewster angle ($\varphi_a = \varphi_B$)

$$(\Delta R/R_1)_B^{(p)} \approx \gamma(\gamma + 2), \quad (3)$$

$$\gamma = (\varepsilon_1(\varepsilon_2 - \varepsilon_a)(\varepsilon_2 - \varepsilon_s)d_2)/(\varepsilon_2(\varepsilon_1 - \varepsilon_a)(\varepsilon_1 - \varepsilon_s)d_1).$$

Thus, the angular spectrum of $(\Delta R/R_1)^{(p)}$ near the Brewster angle has an approximately Lorentzian profile with the full width at half-maximum $2\delta_B$. The half-width of the angular spectrum does not depend on the parameters of the second nanometer layer. Consequently, if the refractive indices of all the media are known, the thickness of the nanometer dielectric layer can be determined relatively easily by measuring near the Brewster angle the angular spectrum of $(\Delta R/R_1)^{(p)}$ caused by depositing any other transparent ultrathin layer on the layer in question.

We then consider determination of the refractive index and the thickness of a nanometer film. To do this we need to include measurements of another independent quantity. In dynamic situations it is convenient to use $(\Delta R_1/R_0)_B^{(s)}$, which is the relative change in the reflection coefficient of s-polarized light from the substrate caused by deposition of the layer under study (layer 1) at the Brewster angle. It is advisable to use s-polarized radiation, because it has a weak angular dependence near φ_B (the angle of incidence need not be determined highly accurately). At the Brewster angle $(\Delta R_1/R_0)_B^{(s)}$ is described by the following expressions within the second order of the small parameters d_1/λ inclusive:

$$\left(\frac{\Delta R_1}{R_0}\right)_B^{(s)} \approx -16\pi^2 \varepsilon_a \varepsilon_s (\varepsilon_a + \varepsilon_s)^{-1} (\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_s)(\varepsilon_s - \varepsilon_a)^{-2} \left(\frac{d_1}{\lambda}\right)^2. \quad (4)$$

From (2) and (4) we conclude that

$$\begin{aligned} \varepsilon_i &= (\varepsilon_a + \varepsilon_s \pm ((\varepsilon_s - \varepsilon_a)^2 + 4\varepsilon_a \varepsilon_s \gamma)^{1/2}) (2(1-T))^{-1}, \\ T &= 4\varepsilon_s^{-2} (\varepsilon_a + \varepsilon_s)^2 \delta_B^2 / (\Delta R_1 / R_0)_B^{(s)}. \end{aligned} \quad (5)$$

3 Absorbing substrate

Let us consider the effect of dielectric nanometer layers on the reflection of linearly polarized light from absorbing massive substrate from the viewpoint of photorefectance diagnostics of such layers. The absorbing substrate *s* is described by the complex dielectric constant $\varepsilon_s - i\xi_s$. In the case of two nanometer films, one can easily obtain by the matrix method of layered media calculation [5] the following expressions for the differential reflectivity $(\Delta R_2 / R_0)^{(s)} \equiv (R_2^{(s)} - R_0^{(s)}) / R_0^{(s)}$ of s-polarized light in the first order in $d_{1,2} / \lambda$:

$$\begin{aligned} \left(\frac{\Delta R_2}{R_0}\right)_B^{(s)} &\approx -8\pi \cos \varphi_a n_a \xi_s ((\varepsilon_s - \varepsilon_a)^2 + \xi_s^2)^{-1} ((\varepsilon_i - \varepsilon_a)(d_1 / \lambda) + \\ &(\varepsilon_s - \varepsilon_a)(d_2 / \lambda)). \end{aligned} \quad (6)$$

For p-polarized light, the angle φ_B appears to be of particular interest as well.

For $\xi_s / |\varepsilon_s - \varepsilon_a| \ll 1$ the absolute value of $(\Delta R_2 / R_0)^{(p)}$ reaches a maximum near this angle. Using the same procedure as for (6), we obtain for $\varphi_a = \varphi_B$:

$$\left(\frac{\Delta R_2}{R_0}\right)_B^{(p)} \approx -8\pi \varepsilon_s^2 (\xi_s (\varepsilon_s - \varepsilon_a)(\varepsilon_s + \varepsilon_a))^{1/2} \sum_{i=1}^2 \varepsilon_i^{-1} (\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_s)(d_i / \lambda). \quad (7)$$

Therefore, the advantage of using the angle φ_B for p-polarized light increases with decreasing ξ_s and increasing ε_s . Thus, the use of p-polarized light incident at the pseudo-Brewster angle is most suitable for semiconductor substrates in the spectral region of their intrinsic absorption.

The approximate expressions are suitable not only for determining the behavior of $(\Delta R_2 / R_0)^{(s,p)}$, i.e., the analysis of the direct problem. They also provide a simple solution of the inverse problem. Firstly, one can measure for a certain oblique angle of incidence the quantities $(\Delta R_2 / R_0)^{(s)}$ and $(\Delta R_2 / R_0)^{(p)}$ (which represent the relative changes of reflectivities for s- and p-polarized light owing to the deposition of an nanometer film under study on a substrate) and calculate ε_i using the formula

$$\begin{aligned} \varepsilon_i &= \varepsilon_a C \sin^2 \varphi_a (C \cos^2 \varphi_a - y_1)^{-1}, \\ C &= (1 - 2\varepsilon_a \varepsilon_s \sin^2 \varphi_a (\varepsilon_s^2 + \xi_s^2)^{-1}) ((\varepsilon_s - \varepsilon_a)^2 + \xi_s^2) D^{-1}, \end{aligned} \quad (8)$$

$$D = (\varepsilon_a - \varepsilon_s \cos^2 \varphi_a - \varepsilon_D)^2 + (\cos^2 \varphi_a - \varepsilon_D \varepsilon_s^{-1})^2 \xi_s^2,$$

where $\varepsilon_D = \varepsilon_s^2 \varepsilon_s (\varepsilon_s^2 + \xi_s^2)^{-1} \sin^2 \varphi_a$ and $y_1 = (\Delta R_2 / R_0)^{(p)} / (\Delta R_2 / R_0)^{(s)}$. Secondly, one can use only $(\Delta R_2 / R_0)^{(p)}$ for normal incidence and oblique incidence and calculate ε_1 by the formula

$$\varepsilon_1 = \varepsilon_a C \sin^2 \varphi_a \cos \varphi_a (C \cos^3 \varphi_a - y_2)^{-1}, \quad (9)$$

where $y_2 = (\Delta R_2 / R_0)^{(p)}_{\varphi_a} / (\Delta R_2 / R_0)^{(p)}_0$. The advantage of these methods is that they provide an unambiguous determination of ε_1 . The disadvantage is that the denominators of formulas (8) and (9) represent differences of two close quantities. As a result, the quantities y_1 and y_2 , which are determined experimentally, should be measured with high accuracy.

4 Acknowledgements

The work was supported in part by the Estonian Science Foundation (grant No. 4205).

References

1. *Optical Characterization of Epitaxial Semiconductor Layers*, ed. by Bauer G., Richter W., (Springer-Verlag, Berlin, 1996).
2. Adamson P., Differential reflection spectroscopy of surface layers on thick transparent substrates with normally incident light, *Opt. Spectrosc.* **80** (1996) pp. 459-468.
3. Tognini P., Geddo M., Stella A., Cheyssac P., Kofman R., Brewster angle technique to study metal nanoparticle distributions in dielectric matrices, *J. Appl. Phys.* **79** (1996) pp. 1032-1039.
4. Adamson P., Photometric diagnostics of ultrathin dielectric layers by the method of differential reflection of light incident at the Brewster angle, *Opt. Spectrosc.* **83** (1997) pp. 154-160.
5. Abeles F., Recherches sur la propagation des ondes electromagnetiques sinusoidales dans les milieux stratifies. Application aux couches minces, *Ann. Phys. (Paris)* **5** (1950) pp. 596-640.

NANOSTRUCTURED $\text{TiO}_2\text{:Tb}_2\text{O}_3$ PHOSPHOR FABRICATED BY SOL-GEL METHOD ON POROUS ANODIC ALUMINA

O. V. SERGEEV, V. E. BORISENKO

*Belarusian State University of Informatics and Radioelectronics
P. Browka 6, 220013 Minsk, Belarus*

R. HEIDERHOFF, L. J. BALK

*Bergische Universität Gesamthochschule Wuppertal
Fachbereich Elektrotechnik, Fachgebiet Elektronik
42097 Wuppertal, Germany*

E-mail: sergeev@nano.bsuir.edu.by

Green phosphors for high-resolution displays were formed from sol-precursors onto porous layers of anodic alumina (Al_2O_3). High-resolution near-field cathodoluminescence study reveals these films treated at relatively low temperatures ($<200^\circ\text{C}$) to show bright luminescence at 480 and 540 nm from 200-300 nm clusters consisting of xerogel globules of about 50 nm in diameter.

1 Introduction

Current development of display technology is limited mainly by conventional high temperature methods of phosphor fabrication resulting in phosphor particles of 3-5 μm . Further particle downsizing would lead to improved screen packing, resolution, light output and lower excitation voltage. Nevertheless, after conventional grinding phosphors demonstrate substantial losses in luminescence efficiency attributed to non-radiative recombination related to surface damages.

Sol-gel method was shown to be a flexible approach providing fabrication of thin films consisting of 40-300 nm particles [1-3], which are indeed promising for production of high-quality phosphor films. Rare earth doped xerogels are characterized by effective monochromatic light emission in different spectral ranges [4]. Furthermore, oxides formed during sol-gel process are more attractive as potential phosphor than traditional sulphides because of their better thermal and chemical stability and lower gassing in vacuum. Immensely used in optics titanium oxide with high refractive index (more than 2.45 [5]) looks to be one of the best matrix material for applications in display technology.

This paper presents low temperature technology, structural and optical properties of terbium-doped titania xerogel films in a porous layer of anodic alumina for fabrication of nanostructured green phosphors.

2 Materials and methods

Initial sol composition was obtained by homogeneous mixing of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ with water and ethanol. Aqueous-alcoholic solution of terbium nitrite-hydrate was added to the initial sol. Final composition with concentration of terbium oxide of 20 wt.% was spin-on deposited at 2000 rpm for 30 s on 2.9 μm sublayer of porous anodic alumina with pores of 120 nm in diameter formed onto Al foil. After each coating the samples were subjected to heat treatment in air. Then, drying at 360 K for 1 h was performed to densify xerogel films and to avoid their cracking. Subsequent annealing at temperature up to 450 K in the conventional furnace was applied to complete the densification process and to form optically activated glass structure. Beside optical activation of terbium ions heat-treatment provides removing of hydroxyl and carbon groups assisting quenching of photoluminescence. The spin-on deposition and annealing procedures were repeated up to ten times to build up the erbium-doped xerogel films inside and on the top of alumina pores.

Luminescent particles were studied with high-resolution cathodoluminescence (CL) based on a scanning near-field optical microscope implemented into the chamber of a scanning electron microscope [6]. It allows analysis not only optical properties, but also rough test of an electroluminescent ability. Detection of CL by a coated glass-fiber probe with nanosize aperture in the optical near-field mode provided spatial resolution less than 50 nm.

3 Results and discussion

Near-field CL investigations of the samples in a probe-scanning mode with excitation by high-energy electrons (15 keV, 12 kHz) resolved the surface topography and NFCL patterns which are shown in Fig. 1. It is clearly seen that the surface of the film is uniformly structured and planarized with a roughness less than 10 nm. Globules with the size of about 50 nm are identified. Such structure is typical for xerogel films covering porous layers. This fact approved as well by prior TEM and RBS measurements indicating completely filled pores by the terbium-containing xerogel. The room-temperature spectrum of intense green emission reveals two bright bands at 480 and 540 nm corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ main transitions of trivalent terbium ions.

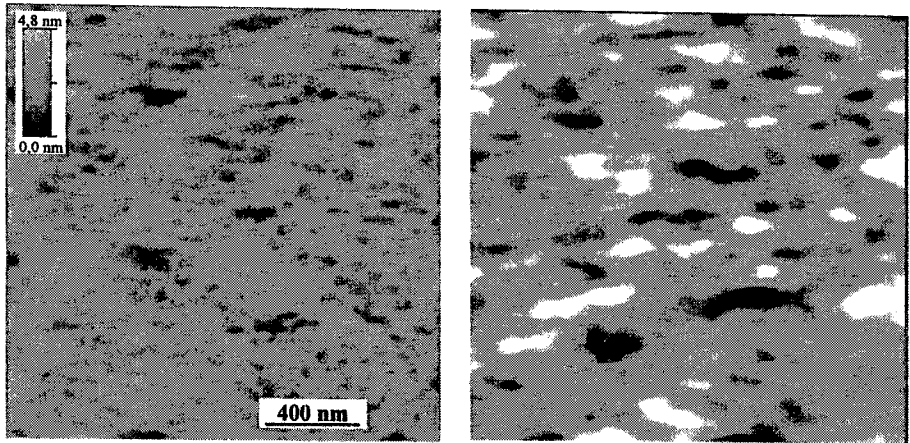


Figure 1. Topography and near-field CL images of terbium-doped titania xerogel film on porous anodic alumina.

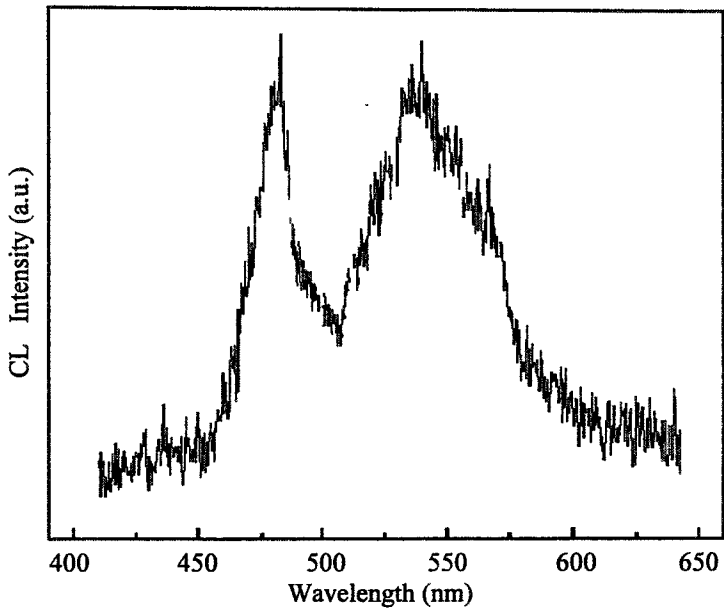


Figure 2. Room-temperature luminescence spectrum of terbium-doped titania xerogel film on porous anodic alumina.

4 Conclusion

A simple low temperature method for fabrication of nanostructured green phosphor has been proposed. Thin films with luminescent particles as small as 50 nm were fabricated by sol-gel method on porous anodic alumina. Evidently, porous layer provides strengthening and uniform structuring of the xerogel films and prevents their cracking. The undoubted advantage of the method is the absence of any surface damages leading to luminescence decay via non-radiative recombination via surface states.

5 Acknowledgements

We thank Dr. N. Gaponenko for fruitful discussions. The work has been partially supported by INTAS-BELARUS 97-0250 research grant.

References

1. Hench L. L., West J. K., The sol-gel process, *Chem. Rev.* **90** (1990) pp. 33-72.
2. Serra O. A., Nassar E. J., Rosa I. L. V., Tb³⁺ molecular photonic devices supported on silica gel and functionalized silica gel, *J. Lumin.* **72** (1997) pp. 263-265.
3. Zhang L., Coffey J., Xu W., Zerda T. W., Luminescent Si nanoparticles in sol-gel matrices stabilized by amino acids, *J. Chem. Mater.* **9** (1997) pp. 2249-2251.
4. Gaponenko N. V., Parkun V. M., Katernoga O. S., Borisenko V. E., Mudryi A. V., Stepanova E. A., Rat'ko A. I., Cavanagh M., O'Kelly B., McGilp J. F., Erbium and terbium photoluminescence in silica sol-gel films on porous alumina, *Thin Solid Films* **297** (1997) pp. 202-206.
5. Gaponenko N. V., Sergeev O. V., Misiewicz J., Gnaser H., Heiderhoff R., Cramer R. M., Balk L. J., Dunbar A., Hamilton B., Erbium photoluminescence in sol-gel derived titanium dioxide films. In *Proc. International Conference on Solid State Crystals '98 "Epilayers and Heterostructures in Optoelectronics and Semiconductor Technology"* (Zakopane, Poland, 1998) pp. 239-242.
6. Cramer R. M., Ebinghaus V., Heiderhoff R., Balk L. J., Near-field detection cathodoluminescence investigations, *J. Phys. D: Applied Physics* **31** (1998) pp. 1918-1922.

THREE-DIMENSIONAL PHOTONIC BAND GAP STRUCTURES DOPED WITH Tb^{3+} IONS

N. V. GAPONENKO

*Belarusian State University of Informatics and Radioelectronics
P. Browka St. 6, 220013 Minsk, Belarus*

V. M. SHELEKHINA, O. A. PROKHOROV, P. A. VITYAZ

*Powder Metallurgy Institute
Platonova St. 41, 220600 Minsk, Belarus*

A. P. STUPAK, A. N. PONYAVINA, S. V. GAPONENKO

*Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus
F. Skaryna Ave. 70, 220072 Minsk, Belarus*

J. C. PIVIN

*Centre de Spectrometrie Nucleaire et de Spectrometrie de Masse
Batiment 108, 91405 Orsay Campus, France*

A. V. MUDRYI

*Institute of Physics of Solids and Semiconductors
P. Browki St. 27, 220027 Minsk, Belarus*

E-mail: gaponen@imaph.bas-net.by

Sol-gel process is shown as a promising synthetic route to fabricate three-dimensional photonic crystals doped with luminescent lanthanides. Using silica and Tb-doped titania sol the colloidal crystals with photonic stop band ranging from 480 to 550 nm have been developed, thus fitting the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$ transition of Tb^{3+} ions. Pronounced inhibition of optical transitions of Tb^{3+} ions was observed.

1 Introduction

Since the first predictions of freezing of spontaneous decay of excited atoms and molecules in photonic band gap structures [1-3] the experimental realization of this phenomenon still remains a challenging problem because of the serious technological obstacles. To observe inhibition of spontaneous decay one needs to embed luminescent atoms, molecules or other species (e.g. nanoparticles or clusters) into a heterogeneous medium with strong periodic modulation of refraction index at the submicron length scale, so-called photonic crystal. Colloidal crystals are considered as prototype mesoscopic structures and templates for development of

photonic crystals for the optical range [4]. Among colloidal structures, solid state silica superlattices known as natural or artificial opals are promising precursors of three-dimensional photonic crystals with full control of spontaneous emission of light [5-10].

Colloidal crystals doped with lanthanide ions are one of the best probe systems for experiments in presently available three-dimensional photonic crystals because of their narrow emission spectrum, long intrinsic lifetime and high quantum yield. Recently, we reported on synthesis and first spectroscopical studies of opal-based photonic crystals containing organic molecules [11], nanocrystals [12], and lanthanides [13]. We demonstrated that the sol-gel method provides a synthetic route towards solid-state three-dimensional lattices of silica and titania with high refractive index modulation [14]. It has also been shown that sol-gel chemistry offers a possibility to generate solid xerogels doped with lanthanides in mesoporous channels of porous matrices revealing strong room-temperature photoluminescence (PL) [15,16].

This paper concerns the synthesis of three-dimensional colloidal crystals with photonic band gap fitting the emission spectrum of Tb^{3+} . We compare PL spectra of terbium either implanted in 3D opal-like colloidal crystal or embedded in it within titania xerogel. We demonstrate that spatial periodicity of the colloidal crystals significantly changes the emission spectrum of terbium in the latter case contrarily to that of colloidal crystals doped with terbium by ion implantation. The results are discussed with the use of the multiple wave scattering theory (TMSW).

2 Theory

Since incident radiation with a frequency near the photonic forbidden band damps rapidly, corresponding emitted radiation from intrinsic layers is strongly attenuated too. This effect is the most significant when the photonic crystal band gap overlaps with the absorption band of luminescent centers. It should be revealed as a luminescent intensity decrease at the long-wave range related to the band gap. The larger is number N_l of layers containing luminescent centers, the more significant is this effect.

Some regards may be done with the use of TMSW, which allows to express the coherent field $\langle E(z) \rangle$ of a monolayer stack in the following form [8]:

$$\begin{aligned}\langle E(z) \rangle &= \exp(ikz) \left(\hat{e} + \sum_{j=1}^N G_j^+ \right), \\ \langle E(-z) \rangle &= \exp(ikz) \left(\sum_{j=1}^N G_j^- \exp\{(j-1)2ikl_m\} \right),\end{aligned}\tag{1}$$

where N is a number of monolayers, G_j are the amplitudes of forward and backward scattering of the j -th monolayer in the presence of others, $\hat{e}$ is the unit

vector along z axis, $k=2\pi/\lambda$, l_M is the intermonolayer distances, $R = |\langle E(-z) \rangle|^2$ [8]. To determine G_j we compose the following system of equations:

$$\begin{aligned} G_m^+ &= F^+ + F^+ \sum_{j=1}^{m-1} G_j^+ + F^- \sum_{j=m+1}^N G_j^- \exp\{(j-m)2ikl_M\}, \\ G_m^- &= F^- + F^- \sum_{j=1}^{m-1} G_j^+ + F^+ \sum_{j=m+1}^N G_j^- \exp\{(j-m)2ikl_M\}. \end{aligned} \quad (2)$$

Solving this system of equations for G_j and substituting them into (1) we can determine the coefficients of coherent transmission and reflection of the stack through the individual monolayer amplitude scattering functions F . These functions we calculate using the quasicrystalline approximation of TMSW.

Using this calculation scheme we can show (Fig. 1), for instance, that for a band gap center of dry opal the intensity relation for excited radiation on the first and on the last monolayers with luminescent centers comprises about 0.97 (when $N_1=2$) and 0.45 (when $N_1=10$).

Thus, the photonic band gap effect is expected to be more pronounced with increase of the number of monolayers containing the luminescent ions, whereas its band-gap position could be shifted by tailoring the size of silica particles and refractive index (n) of the medium in the voids. These both parameters could be varied by exploiting the sol-gel synthesis of photonic colloidal crystals.

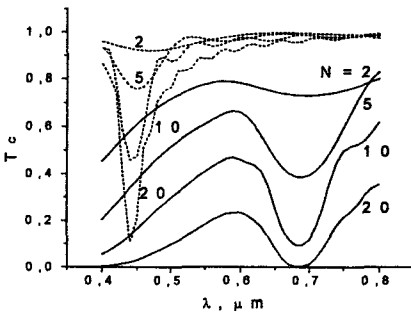


Figure 1. Coherent transmission spectra T_c of a dry opal system (dashed line) and a filled with TiO_2 ($n=2$) one (solid line for different quantity of layers N [$\eta=0.6$, $d=0.2 \mu\text{m}$]), where η is the overlapping factor, d is particle diameter, $T_c = |\langle E(z) \rangle|^2$.

3 Experimental

Tetraethylorthosilicate, ethanol, distilled water, and ammonium hydroxide were used to fabricate a suspension of monodisperse silica globules following the method by Stoerber et al. [17]. To get robust colloidal crystals the suspension of silica globules has been processed employing a centrifugal field at acceleration 8000 m/s^2 . Then the samples were annealed at 900°C in air. Scanning electron microscopy observations reveal that the polycrystalline colloidal structure is made of the grains about 0.1 mm in size consisting of monodisperse silica globules with diameter about 200 nm (Fig. 2). The fabricated samples were cylinders of size 10 mm size

with a flat iridescent top plane, bearing the resemblance with so-called artificial opals [8].

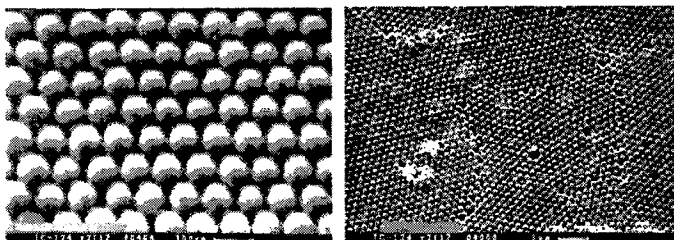


Figure 2. Scanning electron images of the silica colloidal crystal surface. The particle diameter is 250 nm.

Tb^{3+} has been chosen for the experiments since it possesses several strong emission lines ranging from 380 to 630 nm originating from the $^5D_4 \rightarrow ^7F_i$ ($i = 3, 4, 5, 6$) transitions. Terbium was introduced in opal specimens either by implantation of 350 keV ions to a dose of $2 \times 10^{16} \text{ cm}^{-2}$ or by impregnation with a Tb-containing titania gel. The titania sol was prepared from $\text{Ti}(\text{OC}_2\text{H}_5)_4$ in a homogeneous phase with water, ethanol and terbium nitrate solution in a concentration giving 2 at. % of Tb in the TiO_2 xerogel [16]. An immersion of the silica sample in this sol followed by drying in air at room temperature resulted in mechanical hardening of the final product, hereafter referred to as colloidal crystal.

4 Results and discussion

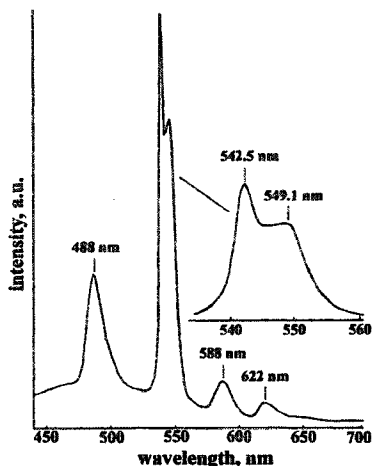


Figure 3. Room-temperature PL spectra of opals implanted with Tb^{3+} .

Tb-implanted opal-like samples reveal at room-temperature four well-resolved PL bands at 488, 543, 588 and 622 nm with a predominant band at 543 nm as it is illustrated in Fig. 3. These bands are typical of $^5D_4 \rightarrow ^7F_j$, $j=3,4,5,6$ transitions of Tb^{3+} derived from colloids [18] or implanted in solids [19]. Contrary to Tb implanted in silica film [19], the main $^5D_4 \rightarrow ^7F_5$ band of Tb^{3+} implanted in silica globules exhibits at room temperature a strong Stark splitting. High resolution (1 nm) spectroscopy allows to detect two lines at 549.1 nm (2.258 eV) and 542.5 nm (2.285 eV). The observed Stark splitting of $^5D_4 \rightarrow ^7F_5$ band in opals is about 3 times greater (6.6 nm or 27.4 meV) than that reported for Tb-doped titania xerogel or polysiloxane films (2 nm or 8 meV) [16,20].

In the case of Tb ion implanted opals the developed surface is shared between the first two layers of silica globules. The ions penetrate the same mean depth of 120 nm in each globule facing directly the beam. The PL of Tb-implanted samples does not exhibit any angular dependence.

Colloidal crystals impregnated with titania xerogel exhibit with pronounced spectrally selective optical reflection and transmission due to the periodic arrangement of silica globules. The spectral position of the reflection peak (stop-band) depends on the globule size and sample orientation (Fig. 4, upper panel). The stop-band fits 545 nm at the incidence angle of about 20° for the chosen size of silica globules.

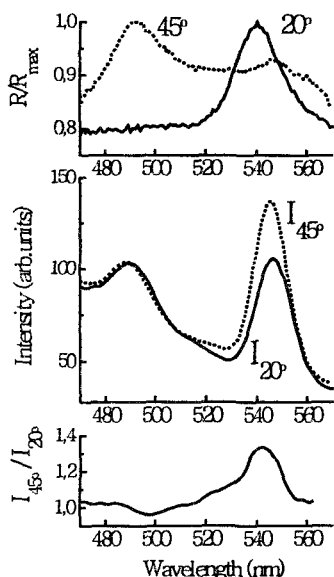


Figure 4. Spectral characteristics of silica colloidal crystals containing Tb^{3+} ions: reflection spectra measured at two different angles of incidence (upper panel); emission spectra measured at two different angles of observation (45° and 20°) (middle panel); ratio of emission intensities measured at 45° and 20° (lower panel).

multiple layers of the crystal on the optical way from excited ions to a detector. Though the final conclusion can be made only on the basis of careful time-resolved studies, strong arguments exist in favor of the inhibition rather than of the filtering effect. The filtering implies that modifications of the emission spectrum follow those of the transmission spectrum of the host colloidal crystal. However, light scattering on the particles is the most significant for the short-wavelength spectral range, whereas in our case the observed partial inhibition of Tb-related PL band at

The samples impregnated with Tb-doped titania gel exhibit, mainly, two strong Tb-related bands: $^5D_4 \rightarrow ^7F_6$ (488 nm) and $^5D_4 \rightarrow ^7F_5$ (543 nm), along with a structureless background of intrinsic emission. The relative weight of these bands depends on the detection angle. When stop-band position fits one of the two Tb^{3+} emission bands the relative intensity of this band diminishes (Fig. 4, middle and bottom). The effect is much stronger for the band located at 545 nm since the stop-band in this range is more pronounced. The decrease in the relative amplitude of the Tb^{3+} emission band resonant with the optical stop band can result from inhibition of spontaneous decay via the relevant quantum transition. This effect is of principal importance from the point of view of quantum optics. It should be revealed not only in the form of the relative amplitude decrease but also as fall of the intrinsic radiative transitions rate via channel whose transition energy is resonant with the stop band.

Alternatively, the observed modification in the emission spectrum can be ascribed to a spectral filtering of emitted light by the

545 nm was predominant contrary to the band at 488 nm. The present data and [7,11] account for the systematic difference in the spectral modification of emission spectra of probes as compared to transmission spectrum of the photonic crystal. Spontaneous emission of probes embedded in a photonic crystal appears to be insensitive to the incoherent contribution to the transmission spectrum. Incoherent contribution to light propagation intrinsically presents under conditions of multiple scattering even in high-ordered three-dimensional structures [6,8]. The observed modification of the emission spectrum correlates with the reflection rather than with transmission spectrum of the host colloidal crystals, thus providing an argument in favor of the effect of photonic density of states upon emission probability versus spectral filtering.

A weak influence of band gap effect on Tb^{3+} ions implanted into opals could be attributed to so-called "surface effects" [21,22]. They relate to complexity of wave vector k for states into the photonic band gap. These surface effects allow radiation to leak on the distances about an inverse value of imaginary part of k . For instance, such effects determine the residual transmission in the photonic band gap when a photonic crystal has a finite size [21], and an interference ripple occurs near the reflection maxima for polycrystal opals [22]. The role of such effects decreases when photonic crystal sizes grow. However, these effects might not be neglected when optical properties of near-surface layers are analyzed.

Therefore, partial relaxation of spontaneous decay inhibition within the photonic band gap at the near-surface layers of photonic crystals could be expected. Perhaps, this circumstance dictates the discrepancies between the angular dependencies of Tb^{3+} PL spectra when terbium was embedded by the two different methods. When Tb was implanted, all luminescence centers were located only within two upper monolayers of silica globules. On the contrary, when sol-gel technology was used, the luminescent centers penetrate about 15-20 monolayers [14]. In the latter case the main part of luminescent centers is located in photonic crystal under the conditions forbidding the most favorable spontaneous decay, and their luminescence spectra correlate with the band gap spectral shift.

5 Conclusion

We synthesized the solid state three-dimensional photonic band gap structure, doped with Tb^{3+} ions and established the angular-dependent modification of Tb^{3+} emission spectrum correlating with the photonic stop band of the host colloidal crystal. Investigation of the photonic band gap effect on spontaneous decay rate will be the subject of forthcoming paper.

6 Acknowledgements

The work has been supported by the grant INTAS-Belarus 97-0250.

References

1. Bykov V. P., *Zh. Eksp. Teor. Fiz.* **62** (1972) 505.
2. Yablonovitch E., *Phys. Rev. Lett.* **58** (1987) 2059.
3. John S., *Phys. Rev. Lett.* **58** (1987) 2486.
4. See special issues on photonic band gap structures: *J. Opt. Soc. Amer. B* **10** (1993), *J. Mod. Opt.* **41** (1994), *J. Lightwave Technol.* **17** (1999).
5. Astratov V. N., Bogomolov V. N., Kaplyanskii A. A., Samoilovich S. M., Vlasov Yu. A., *Nuovo Cim.* **17** (1995) 1349.
6. Bogomolov V. N., Gaponenko S. V., Kapitonov A. M., et al., *J. Appl. Phys. A* **63** (1996) 613.
7. Megens M., Wijnhoven J., Lagendijk A., Vos W., *J. Opt. Soc. Amer. B* **16** (1999) 1403.
8. Bogomolov V. N., Gaponenko S. V., Germanenko I. N., et al., *Phys. Rev. E* **55** (1997) 619.
9. Miguez H., Lopez C., Meseguer F., Blanco A., Vazquez L., Mayoral R., Ocana M., Fornes V., Mifsud A., *Appl. Phys. Lett.* **71** (1997) 1148.
10. Romanov S. G., Sotomayor Torres C. In *Handbook of Nanostructured Materials and Nanotechnology*, ed. by Nalwa H. S. (Academic Press, Orlando, 2000) pp. 231–323.
11. Petrov E. P., Bogomolov V. N., Kalosha I. I., Gaponenko S. V., *Phys. Rev. Lett.* **81** (1998) 7780.
12. Gaponenko S. V., Kapitonov A. M., Bogomolov V. N., Prokofiev A. V., Eychmuller A., Rogach A. L., *JETP Lett.* **68** (1998) 142.
13. Gaponenko S. V., Bogomolov V. N., Petrov E. P., et al., *J. Lightwave Technol.* **17** (1999) 2128.
14. Kapitonov A. M., Gaponenko N. V., Bogomolov V. N., Prokofiev A. V., Samoilovich S. M., Gaponenko S. V., *Phys. Stat. Sol. A* **165** (1998) 119.
15. Gaponenko N. V., Parkhun V. M., Katernoga O. S., et al., *Thin Solid Films* **297** (1997) 202.
16. Gaponenko N. V., Davidson J. A., Hamilton B., Skeldon P., Thompson G. E., Zhou X., Pivin J. C., *Appl. Phys. Lett.* **21** (2000) 1006.
17. Stoeber W., Fink A., Bohn E., *J. Colloid Interface Science* **26** (1968) 6269.
18. Wakefield G., Keron H. A., Dobson P. J., Hutchison J. L., *J. Phys. Chem. Solids* **60** (1999) 503.
19. Amekura H., Eckau A., Carius R., Buchal Ch., *J. Appl. Phys.* **84** (1998) 3867.
20. Gaponenko N. V., Sergeev O. V., Borisenko V. E., et al., *Mater. Sci. Eng.* (to be published).
21. Vlasov Yu. A., Deutsch M., Norris D. J., *Appl. Phys. Lett.* **76** (2000) 1627.
22. Shung K. W.-K., Tsai Y. C., *Phys. Rev. B* **48** (1993) 11265.

EUROPIUM PHOTOLUMINESCENCE IN SOL-GEL DERIVED TITANIA XEROGEL ON POROUS ANODIC ALUMINA

I. S. MOLCHAN, V. I. PACHININ

*Belarusian State University of Informatics and Radioelectronics
P. Brovka, 6, 220013 Minsk, Belarus*

J. MISIEWICZ, R. KUDRAWIEC

*Institute of Physics, Wrocław University of Technology
Wybreze Wyspińskiego 27, 50-370 Wrocław, Poland*

G. E. THOMPSON, P. SKELDON

*Corrosion and Protection Centre, University of Manchester Institute of Science and
Technology
Manchester M60 1QD, United Kingdom*

L. P. MILESHKO

*Taganrog State University of Radioengineering
44 Nekrasovsky, GSP-17A, 347928 Taganrog, Russia*

E-mail: molchan@nano.bsuir.edu.by

Sol-gel derived TiO_2 films containing 40 wt. % Eu_2O_3 were fabricated onto porous anodic alumina by spin-on deposition. Strong room temperature europium photoluminescence, with a maximum at 617 nm, was observed. The dependence of photoluminescence intensity on xerogel amount and temperature has been revealed.

1 Introduction

Recently, fabrication of thin films doped with optically active lanthanides has received considerable attention due to the high quantum efficiency, the narrow width of spectral lines, and weak temperature quenching. Luminescence of lanthanides covers the ultraviolet (Ce), visible (Tb, Eu), and infrared (Er, Nd) spectral range.

Sol-gel processing is a potential way for creation of lanthanide-doped thin films. In the sol-gel process, a solid microporous structure, so called xerogel, is formed. Xerogels are optically transparent, and their chemical content may be varied by preparing the appropriate mixture of sol and solutions of salts. Further, the sol-gel technology is low-cost in comparison with "dry" technologies.

Recently we reported on strong room-temperature Er, Tb and Eu luminescence from sol-gel derived films [1-3]. To enhance the luminescence intensity, originating from sol-gel derived host, it was proposed to use the regular structure of porous

anodic alumina as a mesoporous template for synthesis of Er- and Tb-doped xerogel films [1,2]. Porous anodic alumina is known to exhibit a regular pore morphology with tailor-made pores at the centres of approximately hexagonal cells [4].

In this paper, we report on europium PL in titania xerogel fabricated in mesoporous anodic alumina.

2 Experimental

Porous anodic alumina of 30 μm thick, with the pore diameter of 100 nm, were fabricated onto aluminum substrates. The sol was deposited onto anodic alumina by spinning at 2700 rpm for 30 s. Further drying in air for 30 min was performed. The deposition and drying stages were repeated for sequential deposition of five and ten xerogel layers. Xerogel films containing 40 wt. % Eu_2O_3 /60 wt. % TiO_2 were investigated.

Low temperature PL measurements were performed in the range from 10 to 300 K.

3 Results and Discussion

PL excitation and PL spectra of Eu-containing xerogel films are shown in Fig. 1(a,b). The maximum PL intensity is observed at an excitation wavelength of 285 nm. The PL spectra represent typical europium luminescence peaks in the investigated spectral range arising from $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions of Eu^{3+} ions. The most intense peak at 617 nm corresponds to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions. Also, other peaks are observed at 593 ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 650, 669 ($^5\text{D}_0 \rightarrow ^7\text{F}_3$) and 699, 703 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$).

PL intensity of Eu ions decreases with increasing numbers of spin-on layers. It was found earlier by TEM investigations that after the first spin-on deposition, the xerogel film was distributed not only at the pore base but also on the pore walls, whereas the main volume of the pores remained unfilled. Further, the effective xerogel thickness was increased within the pore volume with an increase in the number of deposited xerogel layers. After approximately 10 spin-on depositions the alumina pores were filled entirely with the xerogel material.

We expect that in our case the porous anodic alumina allows fabrication of a Eu-doped luminescent xerogel film about 30 μm thick. Thus, the structure reveals strong red luminescence, visible to the naked eye at room temperature. The full width at half maximum of the main optical transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 617 nm is 11 nm. Low temperature measurements (Fig. 1(c)) show increasing PL intensity with decreasing temperature. Temperature quenching does not exceed a factor of 5 in the temperature range from 10 to 300 K.

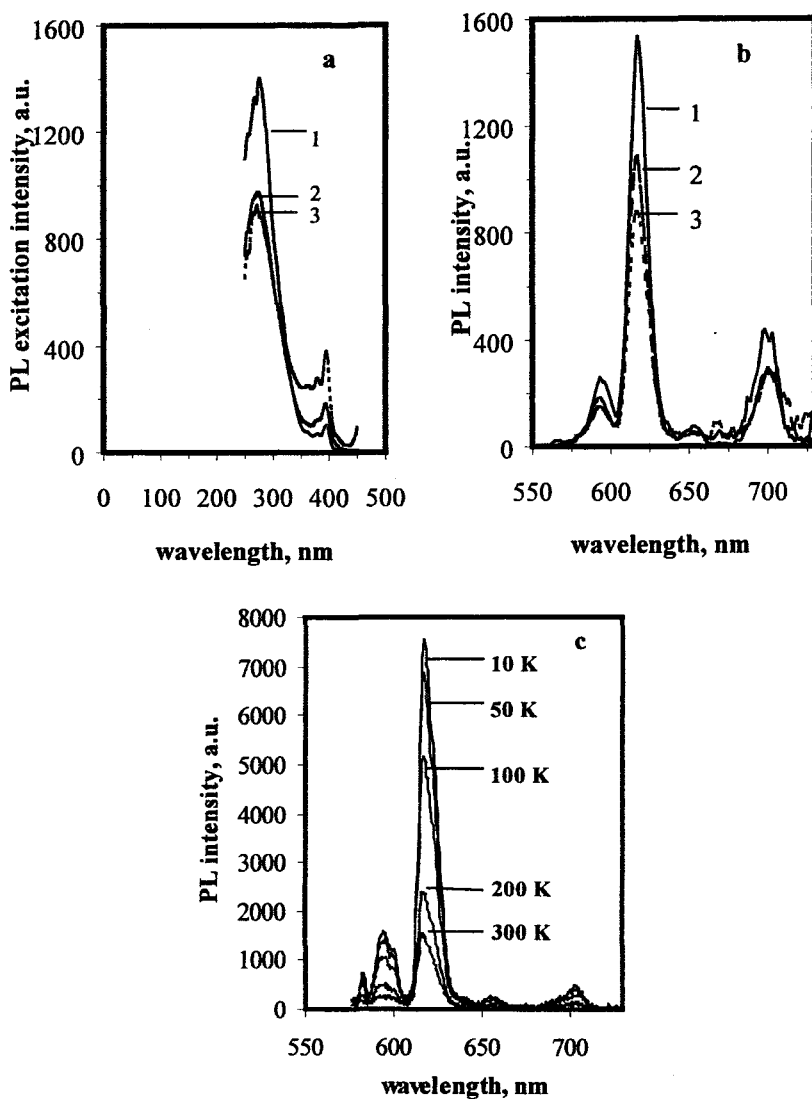


Figure 1. Excitation (a), photoluminescence (b) spectra of europium-doped titania xerogel in porous anodic alumina registered at room temperature: 1 – one spin-on deposition, 2 – five spin-on depositions, 3 – ten spin-on depositions, (c) – temperature dependence of PL for the sample with one spin-on deposition.

4 Conclusion

Sol-gel derived titania xerogel films doped with Eu were fabricated on 30 μm thick porous anodic alumina. The films exhibit strong room temperature PL associated with Eu ions in the xerogel, with a predominant band at 617 nm. By contrast to Tb and Er, subsequent deposition of several xerogel layers within the alumina pores gave an almost two-fold decrease of Eu PL. However, even after the first deposition of the Eu-doped xerogel layer on porous anodic alumina, the structure reveals strong red luminescence visible to the naked eye. Low temperature measurements show insignificant temperature quenching of PL. Experiments aimed at enhancing Eu PL by exploiting the flexible technologies of anodic alumina and xerogel fabrication are in progress.

5 Acknowledgements

This work was partially supported by the grants INTAS-Belarus 97-0250. We thank N. Gaponenko and V. Borisenko for stimulating discussion, and E. Stepanova, A. Stupak, A. Poznyak, S. Lazarouk for technical help.

References

1. Gaponenko N. V., Parkun V. M., Katernoga O. S., Borisenko V. E., Mudryi A. V., Stepanova E. A., Rat'ko A. I., Cavanagh M., O'Kelly B., McGilp J. F., Erbium and terbium luminescence in silica gel film on porous alumina, *Thin Solid Films* **297** (1997) pp. 202-206.
2. Gaponenko N. V., Davidson J. A., Hamilton B., Skeldon P., Thompson G. E., Zhou X., Pivin J. C., Strongly enhanced Tb luminescence from titania xerogel solids mesoscopically confined in porous anodic alumina, *Appl. Phys. Lett.* **76** (2000) pp. 1006-1008.
3. Sergeev O. V., Gaponenko N. V., Mudryi A. V., McGilp J. F., Misiewicz J., Europium Photoluminescence in Sol-Gel Derived Alumina Films. In *Proc. the 8th International Conference "Advanced Display Technologies"* (October 10-14, 1999, Crimea, Ukraine) pp. 179-183.
4. Thompson G. E., Porous anodic alumina: fabrication, characterisation and applications, *Thin Solid Films* **297** (1997) pp. 192-201.

DYNAMIC OBSERVATION AND STRUCTURE ANALYSIS OF NANOSTRUCTURES OF Cu ON Si(111) BY LOW ENERGY ELECTRON MICROSCOPY

T. KOSHIKAWA, T. YASUE

*Fundamental Electronics Research Institute and Academic Frontier Promotion Center
Osaka Electro-Communication University
18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan*

M. JALOCHOWSKI

*Institute of Physics, University of Marie Curie-Sklodowska
pl M. Curie-Sklodowskiej 1, PL 20-031 Lublin, Poland*

E. BAUER

*Department of Physics and Astronomy, Arizona State University
Tempe, AZ 85287-1504, USA*

E-mail: kosikawa@isc.osakac.ac.jp

The growth of Cu on clean and hydrogen-terminated Si(111) surfaces is studied *in situ* by low energy electron microscopy (LEEM). After completion of the "5x5" layer not only regular-shaped three-dimensional islands reported before are observed but also irregular-shaped two-dimensional islands. On the hydrogen-terminated Si(111) surface the formation of the "5x5" structure is suppressed and nanoscale islands are formed preferentially at the step edges and domain boundaries. This is attributed to the enhancement of the surface migration of Cu atoms by the elimination of the surface dangling bonds. Many LEED spots from the nanoislands move with electron energy, which indicates that the islands are faceted. From the analysis of the LEED pattern it is concluded that the nanoislands are the (111)-oriented β -phase Cu-Si compound and are terminated by (111), {5 5 4} and {15 16 13} faces.

1 Introduction

The modification of growth processes on semiconductor surfaces due to elimination of dangling bonds by hydrogen atoms has been studied repeatedly [1]. For example, an epitaxial flat Ag film is formed on the hydrogen-terminated Si(111) surface [2,3]. In the case of Si on Si(100) surface, however, epitaxial growth is prevented by the presence of hydrogen atoms at the interface [4]. This shows that the growth behavior on the hydrogen-terminated surface is not simple, so that further investigations are required. In the present study, Cu was examined. Ag and Cu are in the same group in the periodic table, but properties of the Cu-Si system are quite different from those of the Ag-Si system. For example, the reactivity of Cu with Si is so high that Cu silicide can easily form even at room temperature [5,6]. Therefore

the modification of the growth processes on a hydrogen-terminated surface in such a reactive system is interesting.

Observation with the microscopic techniques, such as LEEM [2], gives direct information on the growth processes. Compared with REM, LEEM has an advantage of distortion-free imaging, so that it is easier to understand the growth processes. In addition, LEED provides structural information. Although STM is also a powerful tool, it is better suited for the investigation of processes on the atomic level, such as nucleation etc. In the present study, we used LEEM to observe the growth of Cu on the hydrogen-terminated Si(111) surface.

The growth of Cu on the clean Si(111) 7x7 surface has been studied previously with various surface analysis techniques [3-12]. At elevated temperatures between 130 °C and 600 °C, the "5x5" structure is formed. The "5x5" structure is a complicated incommensurate structure, but is a stable phase. It has been reported that triangular and elongated islands are formed on the "5x5" structure [3,12]. The suppression of the formation of the "5x5" structure that might lead to island formation directly on the substrate is one first step to modify the growth process. On an ideal hydrogen-terminated surface, there are no dangling bonds. Therefore, it is expected that the reaction of Cu with Si should be strongly suppressed and surface migration might be enhanced. Then three-dimensional island growth could take place directly.

In the present paper, we will discuss the modification of the growth process of Cu on the hydrogen-terminated surface [13,14]. The structure of the islands formed on the hydrogen-terminated surface as derived from their LEED patterns will be also discussed.

2 Experimental

The growth processes were observed in a compact LEEM. The details of the instrument have been described elsewhere [9]. All LEEM images shown in the present paper are obtained with the (00) beam. The diameter of the contrast aperture was 20 μm .

The specimen used was a B-doped ($> 7000 \Omega\text{cm}$) p-type Si(111) wafer. The sample was flashed by passing direct current through it. After flashing, a sharp 7x7 LEED pattern was observed, and clear contrast of monoatomic steps on the surface was observed by LEEM. Atomic hydrogen was produced using a W filament placed at about 75 mm from the specimen. The temperature of the W filament was kept at about 1500 °C in order to avoid the sublimation of W. In fact, we have observed surface contamination from sublimation of W at about 1800 °C. After exposure to atomic hydrogen, the δ 7x7 LEED pattern was observed at all temperatures used. Cu was evaporated from a BN crucible, at the deposition rate of about 0.55 ML/min. This deposition rate was estimated from the completion of the Cu/Si(111) "5x5" structure at 1.3 ML [5]. During observation of the LEEM images

of the hydrogen-terminated surface, electron stimulated desorption of hydrogen may occur. In order check this, a hydrogen-terminated surface was exposed to a 7 eV electron beam for about 12 h at room temperature. The LEEM image after irradiation was essentially the same as that before irradiation, and the intensity distribution in the fractional order spots of the δ 7x7 structure in the LEED patterns was not different before and after irradiation. Therefore, we conclude that there is no significant electron-stimulated desorption during observation of the growth processes.

3 Results and discussion

3.1 Growth of Cu on the clean surface

It is well established that the growth mode of Cu on the Si(111) surface at temperatures between 130 and 600 °C is of the Stranski-Krastanov type [5,6]. The first layer is completed at around 1.3 ML, and the surface shows the "5x5" reconstruction [5,6,10-15]. The LEEM observations of the formation of the "5x5" structure at different substrate temperatures are shown in Figs. 1 and 2. The substrate temperature was about 600 °C in Fig. 1 and about 380 °C in Fig. 2.

Fig. 1(a) shows the LEEM image of the clean Si(111) 7x7 surface in which clear monoatomic steps and the domain boundaries of the 7x7 structure between steps can be seen. With increasing coverage, dark areas develop along steps. The dark areas are identified as the "5x5" structure. The "5x5" structure spreads across both upper and lower terraces. This type of growth has been already observed by LEEM [17] and REM [16].

Fig. 1(b) shows the initial nucleation and growth of the "5x5" structure. There are many small dark "5x5" areas along the step edges. The narrow part is the boundary of the adjacent "5x5" domains. On the wide part there is always the end of a domain boundary of the original 7x7 surface as shown in the inset. This indicates that the nucleation of the "5x5" structure takes place preferentially at the

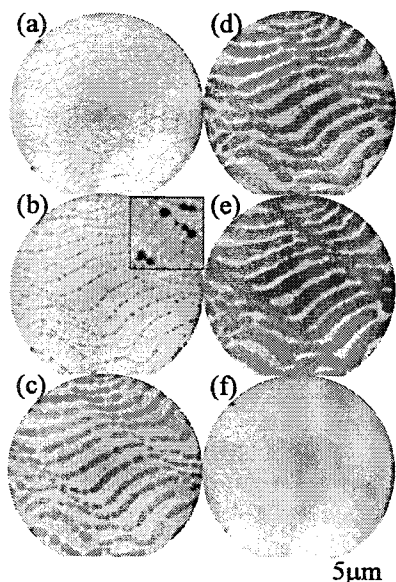


Figure 1. Formation of Cu/Si(111) "5x5" structure at around 600 °C. The coverage is (a) 0 ML, (b) 0.1 ML, (c) 0.5 ML, (d) 0.7 ML, (e) 0.9 ML, (f) 1.4 ML. $E_p = 10.4$ eV. The inset figure in Fig. 1(b) shows a magnified image of the left-bottom of the figure.

intersections of the domain boundaries of the 7x7 structure with the steps which are a defect sites on the surface. The deposited Cu atoms migrate on the clean 7x7

surface and are trapped at defect sites such as step edges and domain boundaries. When the density of the trapped Cu atoms becomes high enough to nucleate, the conversion from 7x7 to "5x5" structure takes place. The number density of Si atoms

in the 7x7 reconstruction is 2.08 ML and that in the "5x5" structure is about 1 ML [12,13]. Then the growth rate toward the upper terrace becomes nearly the same as that toward the lower terrace [16]. With further Cu deposition, the individual dark "5x5" regions grow together as shown in Fig. 1(c-e). This indicates preferred growth along the steps. Fig. 1(f) shows the LEEM image after completion of the "5x5" structure. There is no clear contrast in the image, so that the surface is now covered completely by the "5x5" layer.

Fig. 2 shows the growth of the "5x5" structure at a lower substrate temperature (about 380 °C). At this growth temperature, the "5x5" areas nucleate not only at the step edges and domain boundaries but also on the terraces between the steps and domain boundaries. The size of the "5x5" domains on the terraces is small, and many "5x5" domains nucleate on the terrace. This can be understood by the shorter surface

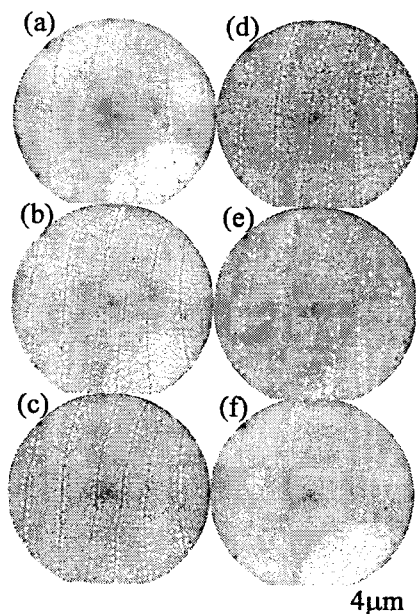


Figure 2. Formation of the Cu/Si(111)"5x5" structure at 380 °C. The coverage is (a) 0 ML, (b) 0.2 ML, (c) 0.5 ML, (d) 0.7 ML, (e) 1.2 ML, (f) 1.4 ML. $E_p=10.3$ eV.

migration distance of the adsorbed Cu atoms on the 7x7 surface at this growth temperature than at the higher growth temperature shown in Fig. 1.

In Fig. 2(c-e), remaining 7x7 areas (bright areas) can be seen along both sides of the step edges, that is a denuded zone. The size of the domains of the "5x5" structure is small and the domains hardly coalesce. This indicates that the orientations of the domain may be different. After completion of the "5x5" structure, three-dimensional islands grow. Three-dimensional islands grown on the "5x5" structure have been already observed by SEM [5] and LEEM/PEEM [17]. In both cases, two types of shapes of islands were observed, a triangular one and an elongated one. It was shown that the edges of islands are parallel to the $\langle 1\bar{1}0 \rangle$ crystallographic directions of the substrate. In the present LEEM study, the same types of islands were observed. In addition, an irregular shaped islands are seen. In order to understand this difference between the triangular, elongated islands and the irregular shaped islands, LEEM images at different electron energies, that is different diffraction conditions, were taken. Fig. 3 shows such a series of LEEM images. The coverage is 10.9 ML, which is the same as that in Fig. 3(b). The

electron energy is (a) 6.2 eV, (b) 11.3 V, (c) 14.6 V and (d) 18.2 V. It is clearly seen that two types of crystals, triangular or elongated and irregular shaped crystals, have a different energy dependence of the contrast. The triangular and elongated islands are seen with dark contrast except Fig. 3(b), which indicates that these islands have tilted top faces. On the other hand, the contrast of the irregular shaped islands strongly depends on the electron energy. In Fig. 3(a), the irregular shaped islands are dark, while white contrast can be seen in Figs. 3(b,d). The irregular shaped islands are hardly seen in Fig. 3(c). From these diffraction contrasts behaviors it can be concluded that the irregular shaped islands are flat and probably have an orientation or structure different from that of the elongated and triangular islands.

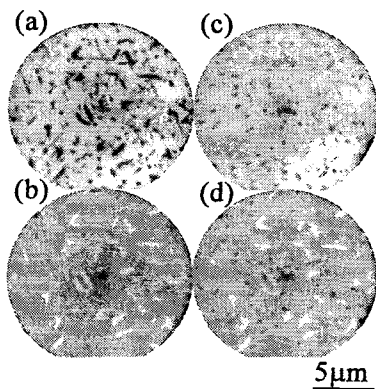


Figure 3. LEEM images of the islands with several energies. E_p = (a) 6.2, (b) 11.3, (c) 14.6 (d) 18.2 eV. The substrate temperature is 380 °C.

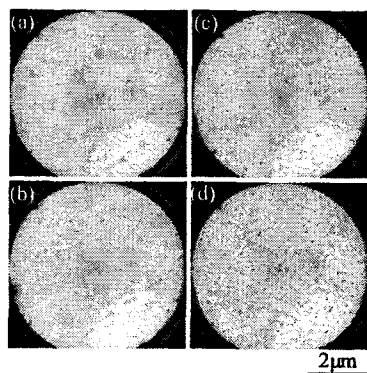


Figure 4. Growth process of Cu on the hydrogen terminated Si(111). E_p = 4.4 eV. The coverage of Cu is (a) 0 ML, (b) 1.1 ML, (c) 2.2 ML, (d) 5.5 ML.

3.2 Growth of Cu with hydrogen

On the hydrogen terminated surface, the growth process of Cu is quite different from that on the clean surface. Fig. 4 shows the growth of Cu on the hydrogen terminated surface. The substrate temperature was about 380 °C. Fig. 4(a) shows the LEEM image of the Si(111) 8×7 surface. In comparison with the LEEM image shown in Fig. 1(a), the contrast of the monoatomic step and the domain boundary is not clear. The weak contrast is mainly due to the following two reasons. One is the diffraction condition which corresponds to the electron energy used. In Fig. 1 the electron energy of about 10 eV is used, while that is 4.2 eV in Fig. 4. The other is the difference in the surface structure. We observed a large number of images of the hydrogen terminated surface, and the contrast was always weak. It is likely that the atomic structure at the step and domain boundaries changes by the hydrogen termination. Since the diffraction intensity is sensitive to the atomic structure, the decrease of the contrast might be induced by the hydrogen termination.

Figs. 4(b-d) show the growth of Cu islands on the hydrogen terminated surface. In Fig. 4(c), the formation of islands can be seen, and the contrast of islands

becomes stronger with increasing coverage as shown in Fig. 4(d). This indicates that the size of islands becomes larger with increasing coverage. The formation of islands can not be seen in Fig. 4(b), because the size of islands is too small to observe the clear contrast. In Fig. 4(d), islands can be seen mainly at the step edges and the domain boundaries. And no contrast due to the "5x5" structure is seen. From this observation, the role of hydrogen appears to suppress strongly the formation of the "5x5" structure.

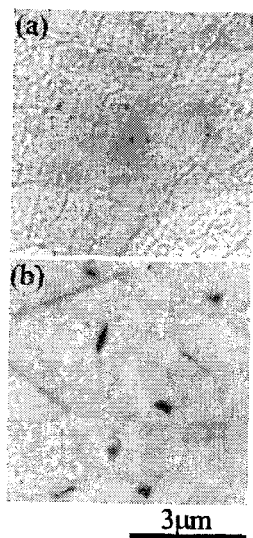


Figure 5. LEEM images of Cu islands formed on the hydrogen terminated Si surface at 4.4 ML. The substrate temperature was (a) 350, (b) 400 °C. $E_p = 4.2$ eV(a), 7.5 eV(b).

Fig. 5 shows the growth of islands on the hydrogen terminated surface at two different substrate temperatures. The substrate temperature is (a) about 350 °C and (b) about 450 °C. Below about 400 °C, the small islands are formed preferentially at the step edges and the domain boundaries as shown in Fig. 5(a). And the number of islands grown on the flat terraces surrounded by steps and domain boundaries increases with reducing the substrate temperature as shown in Fig. 4(d) and Fig. 5(a).

Above 400 °C, the shape and size of islands is different from those below that temperature, as shown in Fig. 5(b). The shape and size is similar to those observed on the clean surface. This indicates that the growth of Cu on the hydrogen terminated surface above 400 °C is nearly the same as that on the clean surface, which is the formation of the "5x5" structure followed by the formation of islands on it. Indeed the LEED pattern showed the formation of the "5x5" structure. The thermal desorption spectrum of hydrogen from the hydrogen terminated Si(111) shows three dominant peaks at around 380, 420 and 550 °C [18]. At the substrate temperature of about 450 °C in Fig. 4(b), many hydrogen atoms should still remain on the surface. The growth process of Cu, however, is similar to that without hydrogen. This experiment suggests that the Cu induced desorption of hydrogen might take place above 400 °C.

3.3 *The structure of the nanoislands on the hydrogen terminated surface*

In order to determine the structure of the nano-islands on the hydrogen-terminated surface, the LEED pattern was observed as a function of coverage. At low coverage clear spots due to the δ 7x7 structure were observed together with weak additional spots from the nanoislands. With increasing coverage the intensity of the δ 7x7 spots decreased while that from the nanoislands increased. The positions of the diffraction spots observed at several electron energies are shown in Fig. 6. The

substrate temperature is about 350 °C. The LEED pattern has a three-fold symmetry and there are two kinds of spots. One is moving along a line connecting the fundamental spots of the substrate, that is along the substrate $\langle 112 \rangle$ directions, and the other deviates from these directions by about 19°. The movement of the spots shows that the nanoislands have inclined faces with different orientations, and there are three equivalent orientations rotated by 120° with respect to each other.

The large solid circles mark spots also from the nanoislands, however these

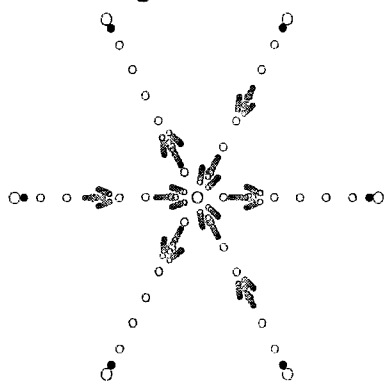


Figure 6. Schematic drawing of the LEED pattern observed at several electron energies. Open circles show spots of the hydrogen terminated Si(111) $\delta 7 \times 7$ surface. The small circles and solid circles indicate positions of the diffraction spots from nanoislands. Ep increases from white (3 eV) to black (10.5 eV) shading in 1.5 eV step.

spots do not move with electron energy. These spots are observed just inside of the first order spots of the substrate at a reciprocal lattice distance from the (00) spot of about $0.285 \text{ \AA}^{-1}$. This distance is incompatible with Cu so that it has to be assigned to a Cu-Si compound. The phase diagram of the Cu-Si system is quite complicated with several compounds [19,20]. The phase which fits best to the solid circles is the body centered cubic β -phase compound with a lattice constant of 0.285 nm [19]. The reciprocal lattice distance of $0.285 \text{ \AA}^{-1}$ agrees within the limits of error with that expected for the (10) spots of a (111)-oriented β -phase crystal (the reciprocal lattice distance is $0.286 \text{ \AA}^{-1}$). The fact that the β -phase forms in the bulk at around 800 °C does not speak against this interpretation because in epitaxy frequently non-equilibrium structures are formed.

The observed angle θ of the (00) beam from an inclined face in a LEEM with a bias voltage of 5000 V is related to the angle θ_0 of the (00) beam and the electron energy V_0 at the sample by $\sin\theta = \sin\theta_0 \sqrt{V_0/5000}$. With this equation we can calculate the angle θ as a function of the inclination angle ϕ of the facet. The angle θ can be deduced from Fig. 6 with reference to the substrate lattice spacing. Fig. 7 shows the relationship between the angle θ and the inclination angle ϕ from the surface normal. Solid circles show the measured angles for the spots moving along $\langle 112 \rangle$ direction and open circles those for the spots moving 19° off these directions. The thick lines show the errors of the measured angles. From this figure we can estimate the inclination angles ϕ are about 7.5° and 5° for two kinds of spots.

The {443} face fits well to the inclination angle of 7.5° and the inclination angle of the {15 16 13} or {14 15 12} face is close to 5° for 19° off-directions. As seen in Fig. 6, a spot along $\langle 112 \rangle$ direction and two spots along 19° off-direction form a triangle. When the angles of the center of the triangle are plotted in Fig. 7, one can determine the average inclination angle of facets. The obtained angle is

about 5.6° that agrees well with that of the $\{554\}$ face. The $\{554\}$ face consists of the (111) terraces and monoatomic steps along the $\langle 110 \rangle$ direction with a separation of 0.814 nm. The step distance of 0.814 nm corresponds to the reciprocal lattice spacing of $0.123 \text{ \AA}^{-1}$. The reciprocal lattice spacing can be also determined from the LEED pattern by using the angle θ for the spots moving along $\langle 112 \rangle$ direction. The reciprocal lattice spacing is about $0.124 \text{ \AA}^{-1}$. This agrees with that of the $\{554\}$ face.

The nanoislands are the β -phase compound as shown above, so that we can

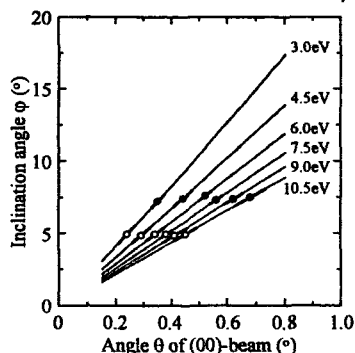


Figure 7. The relationship between the observed angle θ of (00) beam from the inclined face and the inclination angle ϕ . Circles show the measured angle θ in the LEED patterns.

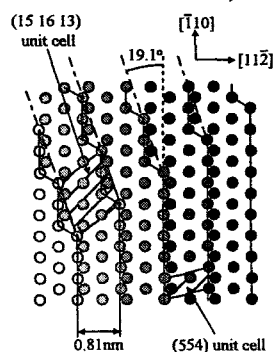


Figure 8. The top view of the atomic arrangement of the (111) -oriented β -phase Cu-Si compound. The solid lines indicate the step toward the $[11-2]$ direction. The step distance is 0.814 nm that corresponds to the $\{554\}$ face. The step configuration for the $(15\ 16\ 13)$ face is also indicated in the upper part of the figure.

draw their atomic arrangement. Fig. 8 shows the top view of the atomic arrangement and solid lines indicate the step edges. The step down direction is the $[112]$ direction and the steps run along the $[110]$ direction. The 19° rotated steps can be drawn to fit to the $\{554\}$ face. In this case the face is the $(15\ 16\ 13)$ face. The inclination angle ϕ of the $(15\ 16\ 13)$ face is 4.9° that agrees well with that determined in Fig. 7. Since the LEED pattern shows a three-fold symmetry, we have to connect the three equivalent atomic arrangements rotated by 120° with respect to each other. Then two or three atomic layer steps can be easily introduced, so that on average $\{443\}$ facet appear. Therefore, it is concluded that the LEED pattern can be explained by $\{554\}$ and $\{15\ 16\ 13\}$ faces of the β -phase Cu-Si compound.

4 Conclusion

The growth of Cu on the clean and hydrogen-terminated Si(111) surfaces was studied *in situ* by LEEM. On the clean surface the well known "5x5" incommensurate structure is formed. The growth of the "5x5" structure depends on

the substrate temperature. At higher substrate temperature, the homogeneous "5x5" layer is formed and 3° rotated equivalent two domains can be recognized in LEED pattern. Many small domains, however, nucleate on the terrace and the domains hardly coalesce at lower substrate temperature. After the completion of the "5x5" structure three-dimensional islands grow. Flat irregular shaped islands are observed in addition to the triangular and elongated islands.

On the hydrogen-terminated surface the growth process is completely different from that on the clean surface. Nanoscale islands decorate the step edges and domain boundaries. The prominent role of the hydrogen termination is the suppression of the formation of the "5x5" structure, and the enhancement of the surface migration of incoming Cu atoms.

The nanoislands are the β -phase compound and have the facet structure consisted of {554} and {15 16 13} faces with step bunches.

5 Acknowledgements

This work was supported by a Grant-in-Aid for Creative Basic Research (09NP1201), a Grant-in-Aid for Scientific Research (10044184) from the Ministry of Education, Science, Sport and Culture. This work was also supported by the Murata Science Foundation.

References

1. See for example, Oura K., Lifshits V. G., Saranin A. A., Zotov A. V., Katayama M., *Surf. Sci. Rep.* **35** (1999) 1.
2. Naitoh M., Shoji F., Oura K., *Surf. Sci.* **242** (1991) 152.
3. Sumitomo K., Kobayashi T., Shoji F., Oura K., *Phys. Rev. Lett.* **66** (1991) 1193.
4. Copel M., Tromp R. M., *Phys. Rev. Lett.* **72** (1994) 1236.
5. Daugy E., Mathiez P., Salvan F., Layet J. M., *Surf. Sci.* **154** (1985) 267.
6. Kemmann H., Müller F., Neddermeyer H., *Surf. Sci.* **192** (1987) 11.
7. Yasue T., Koshikawa T., Jalochowski M., Bauer E., *Surf. Rev. Lett.* **7** (2000) -in press.
8. Yasue T., Koshikawa T., Jalochowski M., Bauer E., *Surf. Sci.* - to be submitted.
9. Adamec P., Bauer E., Lencová B., *Rev. Sci. Instrum.* **69** (1998) 3583.
10. Zegenhagen J., Fontes E., Grey F., Patel J. R., *Phys. Rev. B* **46** (1992) 1860.
11. Mortensen K., *Phys. Rev. Lett.* **66** (1991) 461.
12. Koshikawa T., Yasue T., Tanaka H., Sumita I., Kido Y., *Surf. Sci.* **331-333** (1995) 506.
13. Koshikawa T., Yasue T., Tanaka H., Sumita I., Kido Y., *Nucl. Instrum. Methods B* **99** (1995) 495.
14. Yamashita K., Yasue T., Koshikawa T., Ikeda A., Kido Y., *Nucl. Instrum. Methods B* **136/138** (1998) 1086.

15. Kawasaki T., An T., Ito H., Ichinokawa T. - to be submitted.
16. Takayanagi K., Tanishiro Y., Ishitsuka T., Akiyama K., *Appl. Surf. Sci.* **41/42** (1989) 337.
17. Mundschau M., Bauer E., Teliaps W., *J. Appl. Phys.* **65** (1989) 4747.
18. Schulze G., Henzler M., *Surf. Sci.* **124** (1983) 336.
19. Hansen M., *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958) 629.
20. Massalski T. B., *Binary Alloy Phase Diagrams. Second Ed.* (ASM International, Ohio, 1990) 1477.

OPTICAL PROPERTIES OF LAYER-PERIODIC METAL NANOPARTICLE SYSTEMS IN THE VISIBLE

S. M. KACHAN, A. N. PONYAVINA

Institute of Molecular and Atomic Physics NASB

F. Skaryna Ave. 70, 220072 Minsk, Belarus

E-mail: lirp@imaph.bas-net.by

The method for calculation of layer-periodic metal nanoparticle structure transmission and reflection is proposed. Correlation effects in close-packed monolayers and size dependence of metal particle optical constants are taken into account. The dependence of spectral characteristics of silver nanosphere monolayers near the surface plasmon frequency has been investigated at various particle concentrations and sizes. The long-wave shift of the plasmon resonance with increasing fitting factor is shown. Formation of the photonic stopband accompanied by variation of a plasmon absorption band structure has been established.

1 Introduction

Planar structures of monodisperse metal nanoparticles are promising materials for linear and non-linear optics, laser physics, optoelectronics. Last years the considerable advance in fabrication of such type of ultradisperse metal-dielectric systems is achieved, and their electrical properties are actively studied. The optical characteristics of such objects are also of great interest due to appearance in the visible and UV regions of plasmon resonances in metal nanoparticles and size dependence of particle optical constants. Surface plasmon features are extremely dependent on particle size, shapes and concentration of particles [1]. These effects can have a collective nature in the case of close-packed nanoparticles. It was experimentally established that the electrodynamic coupling transforms a structure of plasmon resonances and has a noticeable effect on their spectral position [1].

An additional way to control spectral features of metal nanoparticles is to arrange particles in space, for example to form a stack of the close-packed monolayers separated by solid intermediate films with the thickness comparable with the wavelength of incident light. The systems formed in this way are similar to 1D photonic crystals.

Photonic crystals based on metal-dielectric structures have been investigated more in detail in the IR range. At the same time the metal photonic crystals can be of interest in spectral range close to the surface plasmon frequency.

The present paper is concerned with theoretical investigation of spectral properties of a stack of close-packed metal particles monolayers separated by dielectric films in the plasmon resonance region.

2 Calculation method

To calculate transmission and reflection coefficients of layer-periodic ultradisperse systems we used the self-consistent field method and the quasicrystalline approximation (QCA) [2] of the theory of multiple wave scattering (TMWS). This approach allows to take into account an interference of waves multiply scattered into the particle system.

For coherent transmission and reflection of a partially ordered monolayer of particles we have:

$$T_M = \left| 1 - \frac{\pi}{k^2} \sum_l \rho (2l+1) (c_l + d_l) \right|^2,$$

$$R_M = \left| -\frac{\pi}{k^2} \sum_l \rho (-1)^l (2l+1) (c_l + d_l) \right|^2.$$

Here c_l and d_l are the complicated expressions of the radial distribution function $g(r)$, surface particle concentration ρ and complex particle refractive index $\tilde{m}$. The size dependence of $\tilde{m}$ has been taken into account in the framework of the model of electron mean free path limitation [1]. It should be noted that for a system of parallel monolayers displaced with equal distances l_M between the centres we need to consider a contribution from the scattered waves by particles of neighbouring monolayer. The coherent field of such system composed from N statistically independent monolayers can be written as

$$\langle E(z) \rangle = \exp(ikz) \left(e + \sum_{j=1}^N G_j^+ \right),$$

$$\langle E(-z) \rangle = \exp(ikz) \left(\sum_{j=1}^N G_j^- \exp\{(j-1)2ikl_M\} \right).$$

Here G_j^+ are the amplitudes of forward and backward scattering for the j th monolayer in the presence of another monolayers. Thus, having determined the coherent field we can obtain coefficients of coherent transmission $T_c = \langle |E(z)|^2 \rangle$ and reflection $R_c = \langle |E(-z)|^2 \rangle$ of the stack.

3 Results and discussion

Using the above algorithm for calculation of coherent transmission T_c and reflection R_c , we have shown that the coherent collective effects in close-packed monolayers of silver particles result in a red shift (with respect to isolated particles) of the plasmon resonance and its enhancement and broadening [3].

In the case of a stack of such monolayers with appropriate thickness of solid intermediate films ($n_m = 1.4$) there is a stopband in the visible range, corresponding

to the formation of the photonic stopband due to the one-dimensional ordering. In Fig. 1 we compare transmission spectra of the three different structures constructed from same monolayers. The first case corresponds to the close-packed stack when monolayers lie on each other. The two other cases are associated with special choice of intermonolayer optical distances. It equals to a half and a quarter of the plasmon peak wavelength, respectively. For the half-wavelength intermonolayer distances we can note the strongly narrowed reflection peak as well as a little broadening and the doublet structure of transparency spectra in the plasmon resonance vicinity. The case of quarter-wavelength films corresponds to the stopband spectral position at the collective plasmon resonance frequency. In this case the minimum transmission and reflection occur.

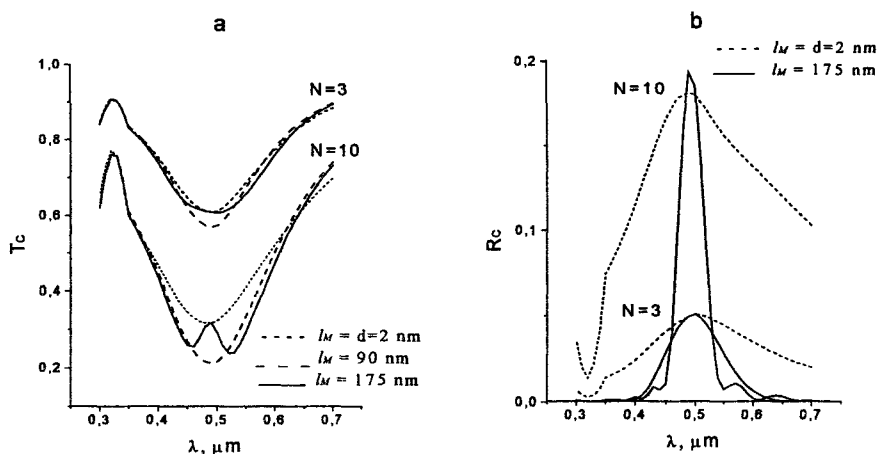


Figure 1. Coherent transmission (a) and reflection (b) of monolayer stacks of silver nanoparticles ($d=2 \text{ nm}$; $\eta = \rho\pi d^2/4 = 0.6$; $n_m = 1,4$) at different distances between monolayer centers, l_m , and number of monolayers N .

For the transmission spectra of the stacks with different intermonolayer distances a blue shift of the doublet structure is expected when intermonolayer distances decrease. But simultaneously there is a quite strong dependence of transmission at λ_0 on intermonolayer distances, with the highest transmission for the case $l_m = 175 \text{ nm}$. The second important issue is the spectral shift of the reflection peak while its intensity remains constant being determined by particle sizes, surface concentration and number of monolayers. Probably, the important factor is a value of monolayer reflection coefficient, which has maximum at the monolayer collective plasmon peak.

The doublet structure and the reflection peak become strongly pronounced when particle size and surface concentration in monolayers grow. That occurs when absolute value of the plasmon absorbance increases. The same effect we can see also when the number of monolayers increases.

4 Conclusions

Attenuation, doublet structure and narrowed reflection peak of the metal nanospheres system in the vicinity of the plasmon resonance in the visible occur under the one-dimensional ordering. Spectral position of these transparency minima and reflectance maxima can be controlled by intermonolayer distances through the plasmon band spectral region. Absolute values of transparency minima and reflectance maxima for such layer-periodical metal nanoparticle system are strongly dependent on particle size, surface concentration and number of monolayers.

5 Acknowledgements

The work was supported by the International Scientific and Technical Center from Grant # B-276.

References

1. Krebig U., Vollmer M., *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).
2. Ponyavina A. N., Silvanovich N. I., Interference effects and spectral characteristics of manylayered scattering systems, *Opt. Spektr.* **76** (1994) pp. 648-655.
3. Kachan S. M., Ponyavina A. N., Optical characteristics of islands films consisted of metal nanoparticles formed in the laser torch plasma. In *Proceedings of III International Conference on Plasma Physics and Technology* (Minsk, Belarus, 2000) **2** pp. 503-507.

CONDUCTANCE QUANTIZATION IN MAGNETIC AND NONMAGNETIC METALLIC NANOWIRES

W. NAWROCKI, M. WAWRZYNIAK

Poznan University of Technology
ul. Piotrowo 3A, 60-965 Poznan, Poland

E-mail: nawrocki@et.put.poznan.pl

We have built a measuring system for investigations on electrical conductance of nanowires. Our measurements concern nanowires formed in both magnetic and nonmagnetic metals. The statistical results (histograms) of the quantization are compared for magnetic and nonmagnetic nanowires. The results of conductance quantization in cobalt nanowires are presented before for the first time.

1 Introduction

We have measured the quantization of the electrical conductance in macroscopic metallic contacts using the method proposed by Costa-Krämer et al. [1]. The quantization phenomenon occurs because of the formation of a nanometer-sized wire (nanowire) between macroscopic metallic contacts in agreements with the theory proposed by Landauer [2]. The measurements concern nanowires formed in both magnetic and nonmagnetic metals.

2 Measuring system

Our measuring system consists of a digital oscilloscope and a function generator connected to computer by an IEEE-488 interface. The block diagram of the measurement system is presented in Fig. 1(a).

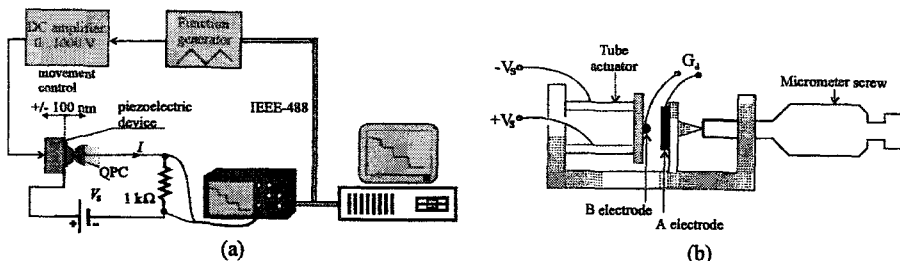


Figure 1. A system for measurements of conductance quantization: (a) instruments; (b) a piezoelectric device for forming nanowires.

The measurement circuit consists of a voltage supply V_s , a pair of gold macroscopic wires which make up the investigated contact, and the resistor R_p . Voltage V_p on a resistor R_p is proportional to the measured conductance G_w . To record V_p , we use a digital oscilloscope LeCroy 93100M with an 8-bit analog-to-digital converter. The oscilloscope is equipped with an IEEE-488 interface. The second circuit is used to control the backward and forward movement of the macroscopic wires between which the nanowires occur. This circuit consists of a digital function generator, a high voltage amplifier and a piezoelectric tube actuator. Fig. 1(b) presents the setup for positioning the electrodes. One of the wires (electrode A) may be moved by the micrometer screw, while the second wire (electrode B) by the tube actuator. Electrode A is horizontal, while electrode B is vertical. Both electrodes are made from wire 0.5 mm in diameter. The investigation has been carried out in air at room temperature. The conductance was measured between two pieces of metal moved to contact by the piezoelectric tube actuator.

3 Conductance quantization in nanowires

Quantization of electric conductance does not depend on the kind of metal and on temperature. However, the purpose of studying quantization for different metals was to see how properties of the metal affect the contacts between wires. For nonmagnetic metals the conductance is described by the Landauer formula [2]:

$$G = \frac{2e^2}{h} \sum_{n=1}^N T_n,$$

where e is the electron charge, h is the Planck quantum, T_n is the electron transmission. Electron spin degeneracy in nonmagnetic nanowires results in the quantum of conductance $G_0 = 2e^2/h$. Removing this degeneracy by a strong magnetic field would make the quantum of electrical conductance equal $G_M = e^2/h$. The effect of the removal of spin degeneracy in nonmagnetic material was experimentally confirmed in the study of quantization of conductance in GaAs/AlGaAs semiconductor subjected to the magnetic field of 2.5 T at 0.6 K [5]. For magnetic metals the conductance formula contains the spin effect [3]:

$$G = \frac{e^2}{h} \left[\sum_{n=1}^{N_\uparrow} T_{n\uparrow} + \sum_{n=1}^{N_\downarrow} T_{n\downarrow} \right],$$

where $T_{n\uparrow}$ is the transmission of electrons with a spin $\uparrow$, $T_{n\downarrow}$ is the transmission of electrons with a spin $\downarrow$.

We have investigated the conductance quantization of nanowires for three nonmagnetic metals (gold, copper and tin) and for one nonmagnetic metal – cobalt. To our knowledge, the results of quantization in cobalt nanowires were not reported before. For nonmagnetic metals, conductance quantization in units of $G_0 = 2e^2/h = (12.9 \text{ k}\Omega)^{-1}$ up to five quanta of conductance was observed for Au-Au, Cu-Cu, Sn-Sn, Au-Cu, Au-Sn, Cu-Sn contacts. The quantization of conductance in our experiment was evident. All characteristics showed the same steps equal to

$2e^2/h$. We observed two phenomena: quantization during breaking contact between two wires, and quantization during making contact between the wires [4]. It should be emphasised that quantum effects were observed only for some of the recorded characteristics. The characteristics are only partially reproducible. They differ in the number of steps and the time length and the height of the steps. The steps can correspond to 1, 2, 3 or 4 quanta.

Conductance quantization has been more pronouncedly observable for gold contacts. Fig. 2(a) shows an example plot of conductance vs time during the process of drawing a gold nanowire (nonmagnetic). Fig. 2(b) shows the conductance histogram obtained from 6000 consecutive characteristics, for the bias voltage $V_{bias} = 0.420$ V.

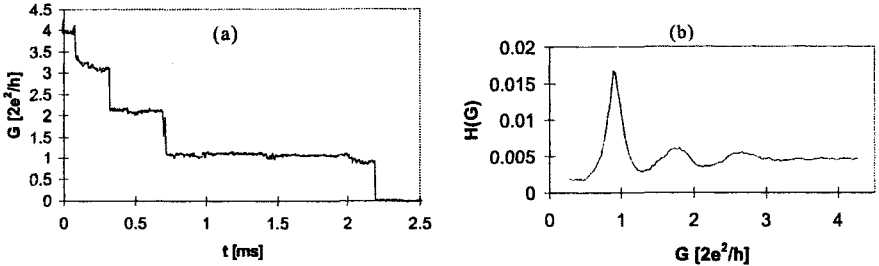


Figure 2. Conductance quantization in gold nanowires: (a) G_d – conductance vs time for $V_{bias} = 0.420$ V at room temperature; (b) histogram from 6000 conductance characteristics.

Fig. 3(a) shows an example plot of conductance vs time during the process of drawing a cobalt nanowire (magnetic material).

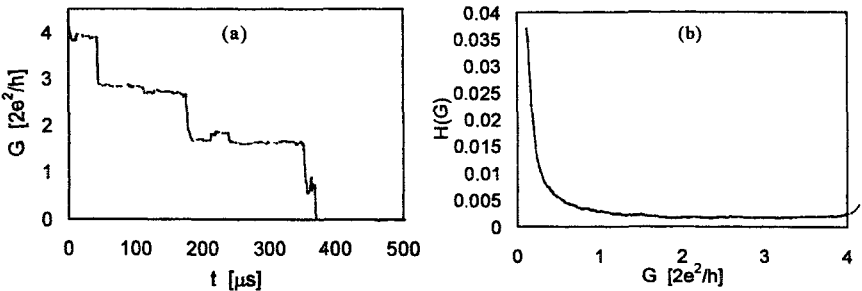


Figure 3. Conductance quantization in cobalt nanowires: (a) G_d – conductance vs time for $V_{bias} = 0.420$ V at room temperature; (b) conductance histogram from 6000 conductance characteristics.

Fig. 3(b) shows the conductance histogram obtained also from 6000 consecutive characteristics, for the bias voltage $V_{bias} = 0.420$ V. This histogram looks quite different from that for gold nanowires. Presented histograms shown that a quantization process in nonmagnetic and magnetic nanowires is different. Fig. 4 shows three histograms for following nanowires: Au-Au, Au-Co and Co-Co.

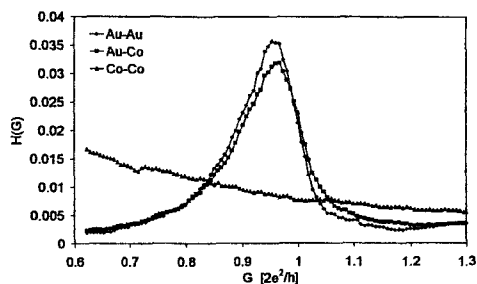


Figure 4. Histograms from conductance characteristics for nanowires: Au-Au, Co-Co and Au-Co.

From Fig. 4 one can conclude that the soft metal (gold) determines properties of nanowires formed by a pair of metals.

4 Conclusions

Conductance quantization has proved to be observable in an experimental setup, giving opportunity to investigate quantum effects in electrical conductivity. Quantization in metallic nanowires occurs to be different for magnetic and nonmagnetic metals. Quantization steps are equal to e^2/h in magnetic nanowires and equal to $2e^2/h$ in nonmagnetic nanowires. We can conclude that the softer metal determines properties of nanowires formed by a pair of metals.

5 Acknowledgements

This work is supported by the research project № 44-1749/KBN at the Poznan University of Technology.

References

1. Costa-Krämer J. L. et al., *Surf. Sci.* **342** (1995) L1144.
2. Landauer R., *J. Phys.: Condens Matter* **1** (1989) 8099.
3. Costa-Krämer J. L., *Phys. Rev. B* **55** (1997) 4875.
4. Martinek J., Nawrocki W., Wawrzyniak M., Stankowski J., *Molec. Phys. Rep.* **20** (1997) 157.
5. van Wees B. J. et al., *Phys. Rev. B* **43** (1991) 12431.

CONDUCTIVITY OF TWO-DIMENSIONAL CHROMIUM AND IRON ORDERED SURFACE PHASES ON Si(111)

N. G. GALKIN, D. L. GOROSHKO, S. TS. KRIVOSHCHAPOV

*Institute for Automation and Control Processes, Far Eastern Department of RAS
Radio 5, 690041 Vladivostok, Russia*

E-mail: galkin@iacp.vl.ru

In situ Hall measurements at room and elevated temperatures of chromium (Si(111) $\sqrt{3}\times\sqrt{3}/30^\circ$ -Cr) and iron (Si(111)2x2-Fe) surface phases are presented. The ultrathin chromium surface phase displays the p-type semiconductor properties with the activation energy of 0.12 eV, while the ultrathin iron surface behaves as a metal with low hole concentration.

1 Introduction

Last years large attention has been given to morphology, atomic and electronic structure of ultrathin epitaxial films of monosilicides and surface phases of chromium and iron on silicon. It is known [1,2] that these films with thickness of 0.1-0.3 nm are often pseudomorphic. Their strained structure results in changes of electrical and optical properties. It has been shown that results of measurements of pseudomorphic films, protected against oxidation by a thin layer of amorphous silicon are not correct [3]. Hence, electrical properties of pseudomorphic films can be investigated only under ultrahigh vacuum conditions (*in situ*). The mechanism of conductivity in pseudomorphic films can be determined only on the basis of wide temperature range Hall measurements in ultrahigh vacuum. The main problem with such measurements is the shunting effect of the silicon substrate. High-temperature measurements of conductivity of two-dimensional surface phases subjected to the substrate shunting effect were not carried out before.

In this paper we present results of *in situ* Hall measurements at room temperature (RT) and at elevated temperatures of chromium (Si(111) $\sqrt{3}\times\sqrt{3}/30^\circ$ -Cr) and iron (Si(111)2x2-Fe) surface phases.

2 Experimental details

The ultrahigh vacuum (UHV) chamber with a base pressure 5×10^{-10} Torr equipped with LEED optics was used for experiments. The metal evaporation unit contained three sublimation sources (Si, Cr, Fe) and a sample holder with a quartz thickness sensor. The built-in UHV Hall unit was supplied with a computer-integrated

measurement system [4]. Silicon p-type, 10 $\Omega\cdot\text{cm}$ (111) wafers were used as substrates. The ordered surface phase $\text{Si}(111)\sqrt{3}\times\sqrt{3}/30^\circ\text{-Cr}$ or $\text{Si}(111)2\times 2\text{-Fe}$ was formed by deposition of thin chromium or iron layer (0.3 nm) on $\text{Si}(111)7\times 7$ substrate at RT followed by annealing at 350 $^\circ\text{C}$ for 30 s. A sharp LEED pattern was seen after this procedure. Hall measurements were carried out first at RT and then at 290–400 K. The linear dependencies of the Hall voltage (U_H) and longitudinal voltage (U_p) on the current through the sample and magnetic induction were shown both for silicon substrates and grown surface phases. Calculations of the sheet conductivity, carrier concentration and carrier mobility in surface phases were carried out within the two-layer model [5,6] with an assumption of homogeneously doped layers.

3 Results and discussion

To investigate conductivity mechanisms in surface phases of metals it is necessary to obtain wide temperature range data on electrical parameters of such systems. Despite some papers dedicated to conductivity of silicon with atomically clean surface have been published [6–8], the mechanism of conductivity at high temperatures is not clear.

The experimental temperature dependence of U_H and U_p for the p-type substrate with an atomically clean surface is shown in Table 1. The temperature increase resulted in rather fast growth of U_p and only slight increase of U_H .

Table 1.

T, K	Si(111)7x7		Si(111) $\sqrt{3}\times\sqrt{3}/30^\circ\text{-Cr}$		Si(111)7x7		Si(111) $\sqrt{3}\times\sqrt{3}/30^\circ\text{-Cr}$	
	$U_H, \mu\text{V}$	U_p, mV	$U_H, \mu\text{V}$	U_p, mV	$\mu, \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$n, \text{cm}^{-2} \cdot 10^{13}$	$\mu, \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$n, \text{cm}^{-2} \cdot 10^{11}$
293	9.35	6.00	9.60	5.85	541	1.85	97	20.0
330	9.40	7.25	9.54	7.32	420	1.86	424	3.75
338	9.42	8.00	9.52	7.62	398	1.90	512	4.27
348	9.40	8.25	9.49	8.00	376	1.88	549	4.40
358	9.45	8.50	9.46	8.38	355	1.92	556	4.62
373	9.50	9.00	9.42	8.95	330	1.86	545	6.31
400	10.7	9.75	9.36	9.71	289	1.60	517	7.58

The hole mobility decreased with temperature, while hole concentration almost did not change up to 370 K and then it slightly decreased. Temperature dependence of the hole mobility can be expressed as $\mu \sim T^{-1.85}$. It is known to be different for oxidized silicon: $\mu \sim T^{-2.7}$ [9]. The difference in the exponent factor may correspond to a reduced of carrier scattering by optical phonons.

Formation of the $\text{Si}(111)\sqrt{3}\times\sqrt{3}/30^\circ\text{-Cr}$ surface phase resulted only in insignificant reduction of the U_p and U_H (Table 1). This tendency is preserved in the whole temperature range studied. Holes were majority carriers in the surface phase. With rising temperature above 320 K the hole concentration and the sheet conductivity slightly increase. The hole mobility did not change too much. Availing the fact that hole mobility in silicon at 290–400 K decreases, we conclude that carriers in the chromium surface phase are submitted to their own scattering mechanism. Activation energy of the hole conductivity is 0.12 eV, thus we can speak about semiconducting character of the chromium surface phase conductivity.

It is known from transmission electron microscopy and microdiffraction [3], that $\text{Si}(111)\sqrt{3}\times\sqrt{3}/30^\circ\text{-Cr}$ surface phase has the lattice parameter precisely $\sqrt{3}$ times larger, than that for the $\text{Si}(111)$ plane. Hence, this phase is considered as a pseudomorphic epitaxial film with a structure similar to CrSi in (111) plane. The facts that chromium and silicon atoms intermix at RT in the layers as thick as 0.01–0.3 nm [10] and hole conductivity is formed in the disordered chromium-silicon layer with Cr thickness of 0.2–0.3 nm [6] also testify to the benefit of such model.

Analyzing the experimental temperature dependence of U_H and U_p presented in Table 2 for iron (0.3 nm) surface phase on silicon one should remember that iron atoms diffuse in silicon already at RT. This was shown by STM [1,11,12], ISS [11], XPS [12], UPS [11], LEED [11,12], RHEED [1]. Moreover, iron forms donor-type surface states in the silicon band gap [7].

Table 2.

T, K	Si(111)7x7		Si(111)2x2-Fe		Si(111)7x7		Si(111)2x2-Fe	
	$U_H, \mu\text{V}$	U_p, mV	$U_H, \mu\text{V}$	U_p, mV	$\mu, \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$	$n, \text{cm}^{-2} \cdot 10^{13}$	$n, \text{cm}^{-2} \cdot 10^{12}$	$\mu, \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$
293	5.41	11.40	5.10	10.01	153	3.25	2.81	246
330	4.26	13.00	4.00	11.37	106	4.12	3.68	167
338	3.96	13.20	4.11	11.83	98	4.43	2.07	243
348	3.80	13.60	3.99	12.19	90	4.62	2.10	241
358	3.71	14.10	4.20	12.69	86	4.73	1.49	302
373	3.76	14.70	4.41	13.45	80	4.67	1.00	357
400	10.7	15.20	4.43	14.07	76	4.14	1.23	245

In our experiments the deposition of about 0.3 nm iron layer and annealing at temperatures 350–500 °C provided observation of the ordered $\text{Si}(111)2\times 2\text{-Fe}$ surface phase. The data of [13] show that $\alpha\text{-FeSi}_2$ film with segregated silicon atoms on the top is synthesized in these conditions and (2×2) superstructure is formed. The $\alpha\text{-FeSi}_2$ film in this thickness range is pseudomorphic and continuous [13]. Breaks of film surface are observed only at annealing temperatures above 600 °C.

The Hall measurements reveal reduction of hole concentration in $\text{Si}(111)2\times 2\text{-Fe}$ surface phase with the temperature increase (Table 2). Hole mobility

slightly changes and does not exceed $300 \text{ cm}^2/\text{V}\cdot\text{s}$, which is higher than that in the silicon substrate at the same temperature. The surface film displays the metal conductivity type with hole concentration $(1-3) \times 10^{12} \text{ cm}^{-2}$.

4 Acknowledgements

This research was performed with financial support of the Russian Foundation of Fundamental Researches (Grant No. 00-02-81000).

References

1. Chevrier J., Le Thanh V., Nitsche S., Derrien J., *Appl. Surf. Sci.* **56-58** (1992) 438.
2. Sirringhaus H., Onda N., Müller-Gubler E., Müller P., Stadler R., von Känel H., *Phys. Rev. B* **47** (1993) 10567.
3. Gasparov V. A., Grazhulis V. A., Bondarev V. V., Bychkova T. M., Lifshits V. G., Galkin N. G., Plusnin N. I., *Surf. Sci.* **292** (1993) 298.
4. Galkin N. G., Ivanov V. A., Konchenko A. V., Goroshko D. L., *Instrum. Experim. Techn.* **42** (1999) 284.
5. Jentzsch F., Froitzheim H., Theile R., *J. Appl. Phys.* **66** (1989) 5901.
6. Galkin N. G., Goroshko D. L., Konchenko A. V., Ivanov V. A., Zakharova E. S., Krivoshchapov S. Ts., *Surf. Rev. Lett.* **7** (2000) 257.
7. Heun S., Bange J., Schad R., Henzler M., *J. Phys.: Condens. Matt.* **5** (1993) 2913.
8. Hasegawa S., Tong X., Takeda S., Sato N., Nagao T., *Progr. Surf. Sci.* **60** (1999) 89.
9. Smith R.A., *Semiconductors*, 2nd ed. (Cambridge Univ. Press, Cambridge, 1978).
10. Plusnin N. I., Galkin N. G., Kamenev A. N., Lifshits V. G., Lobachev S. A., *Phys. Chem. Mech. Surf.* **9** (1989) 55.
11. Alvarez J., Vazquez de Parga A. L., Hinarejos J. J., de la Figuera J., Michel E.G., Ocal C., Miranda R., *Phys. Rev. B* **47** (1993) 16048.
12. Raunau W., Niehus H., Schilling T., Comsa G., *Surf. Sci.* **286** (1993) 203.
13. Sorotti F., DeSantis M., Jin X., Rossi G., *Phys. Rev. B* **49** (1994) 11134.

EFFECT OF THE SYMMETRY ON THE PROPERTIES OF SUPERCONDUCTOR/NORMAL METAL NANOSTRUCTURES

V. N. KUSHNIR

*Institute of Nuclear Problems, Belarusian State University
Bobruiskaya 11, 220050 Minsk, Belarus*

A. YU. PETROV, S. L. PRISCHEPA

*Belarusian State University of Informatics and Radioelectronics
P.Browka 6, 220013 Minsk, Belarus*

E-mail: aleks@gw.bsuir.unibel.by

A. ANGRISANI ARMENIO, C. ATTANASIO, L. MARITATO

*Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia
Università degli studi di Salerno
Baronissi (Sa) I84081 Italy*

E-mail: maritato@sa.infn.it

The effect of symmetry and boundary conditions on the critical parallel magnetic field $H_{c2||}$ in superconductor/normal metal (S/N) nanostructures has been examined both experimentally and theoretically. The $H_{c2||}$ versus temperature (T) dependence was strongly influenced by the sample symmetry plane position. Regard of the symmetry effect allows to determine more definitely parameters of any model describing the superconducting state of S/N superlattices.

Theoretical descriptions of superconducting layered structures are usually based on the analysis of an infinite stack of bilayers which, disregarding the boundary conditions and the actual symmetry of the systems, do not correspond to the experimental situation. Recently, as an example, it has been shown, that the boundary conditions at the edges of the sample completing by the same one at S/N interfaces could play an important role in the $H_{c2||}(T)$ dependencies [1,2].

We experimentally and theoretically investigated the influence of the symmetry of the samples (i.e. whether the symmetry plane is situated in S or in N layer) and of the boundary conditions both at the edges of the sample and at the S/N interfaces on the shape of the $H_{c2||}(T)$ curves. A simple way to vary the symmetry of the multilayer system is to fabricate samples with different number of bilayers N_L . We have deposited Nb/Cu multilayers with identical copper (d_N) and niobium (d_S) thickness, $d_N = d_S \approx 200$ Å, identical Cu and Nb properties. The samples have been fabricated by means of triod dc sputtering technique [3].

We stress that both the investigated samples KS9 and KN10 were obtained in the same deposition run, that allows us to assume the same niobium properties and the same Nb/Cu interface properties. The only difference between these two

samples is the different number of bilayers and, consequently, the different symmetry of the samples. For the sample KS9 $N_L=9$ and for the sample KN10 $N_L=10$, which means that the symmetry of KS9 lies in the middle of S layer while the symmetry center of KN10 falls in the middle of N layer as it shown in Fig. 1.

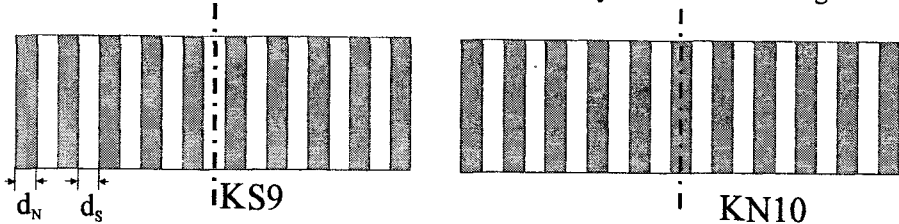


Figure 1. Sketch of the investigated samples with different symmetry plane positions.

Magnetoresistance measurements with a standard four probe technique have been performed for both parallel and perpendicular magnetic fields. The samples were simultaneously mounted in the Oxford insert with the possibility to rotate them in the liquid helium bath. The accuracy of the rotation angle was $\pm 0.1^\circ$. Magnetic field was created by a superconducting solenoid. The H_{c2} values were extracted from the 50 % R_N criterion of the $R(T)$ curves, where R_N is the normal state resistance of the sample just above the transition to the superconducting state. The transition widths ΔT_c in the parallel magnetic field were always less than 0.3 K at fields higher than 2 T, confirming the high quality of the samples. From the $H_{c2\perp}(T)$ and $H_{c2\parallel}(T)$ curves we have calculated in a usual way [4] the values of perpendicular $\xi_{\perp}(0)$, parallel $\xi_{\parallel}(0)$ coherence lengths and the anisotropy parameter $\gamma_0 = \xi_{\parallel}(0)/\xi_{\perp}(0)$ reported in Table 1.

Table 1. Characteristics of the investigated samples. γ_0 is the sample anisotropy at zero temperature.

Sample	N_L	T_c , K	$\xi_{\parallel}(0)$, Å	γ_0	Plane symmetry
KS9	9	6.2	114	2.4	In S layer
KN10	10	5.8	157	2.6	In N layer

In Fig. 2 we present the temperature dependencies of $H_{c2\parallel}$ for both samples. An unusual character of $H_{c2\parallel}(T)$ curve for the sample KS9 is clearly seen, while the $H_{c2\parallel}(T)$ curve for the sample KN10 reflects the "conventional" H - T phase diagram for S/N multilayers [5].

To analyze briefly the actual situation we will follow the standard procedure for determining the parallel critical field applying the boundary problem [1,6] for the equation

$$\left(\nabla - i \frac{2\pi}{\Phi_0} A(\mathbf{r}) \right)^2 \Psi(\mathbf{r}) + \eta(z) \Psi(\mathbf{r}) = 0 \quad (1)$$

with a step function coefficient $\eta(z) = \eta_{S(N)}(T)$ inside the S or N layer, respectively; Φ_0 is the flux quantum; $A(\mathbf{r})$ is the vector potential, which we present in the form $A = (Hz, 0, 0)$. We chose the following coordinate system: the XY plane is parallel to the layer surfaces and coincides with the symmetry plane of S/N structure, the Z axis is directed at right angle to the surface of the layers, the external magnetic field H is oriented along the Y axis. Then, separating the variables in (1), $\Psi(\mathbf{r}) = e^{ikx}\psi(z)$, we obtain

$$\left\{ \frac{\partial^2}{\partial z^2} + \eta(z) - H_0^2 \cdot (z - z_0)^2 \right\} \psi(z) = 0, \quad (2)$$

where $z_0 \equiv k/H_0$ and the notation $H_0 \equiv 2\pi H/\Phi_0$ is introduced for the sake of convenience.

The boundary conditions are set in the following way:

$$\psi(z \rightarrow \pm\infty) \rightarrow 0, \quad (3)$$

for infinite superlattice, or

$$\left. \frac{\partial \psi}{\partial z} \right|_{-L/2} = \left. \frac{\partial \psi}{\partial z} \right|_{+L/2} = 0, \quad (3')$$

taking into account a finite multilayer dimensions (L is the multilayer thickness).

Eq.(2) is supplemented also by the conditions at the S/N interface [7]

$$\frac{1}{\psi} \cdot \left. \frac{\partial \psi}{\partial z} \right|_S = P \cdot \frac{1}{\psi} \cdot \left. \frac{\partial \psi}{\partial z} \right|_N, \quad (4)$$

where P is the boundary transparent coefficient.

We assume traditionally [4] that $\eta_S(T) = 1/\xi_{S0}^2 \cdot (1 - T/T_S)$ and $\eta_N(T) = -1/\xi_{Nc}^2 \cdot T/T_c$, where ξ_{S0} is the coherence length in S layer at zero temperature, ξ_{Nc} is the coherence length in N layer at the critical temperature and T_S is the critical temperature for the bulk superconductor. The solutions of (2) are built according to the standard approach which is based on the routine and clumsy procedure of sequential joining of solutions of Eq. (4) in N and S layers. The maximum value of the external magnetic field parameter $H_{0\max}$ for which the condition (3') is satisfied is the upper critical field. The dependence of $H_{0\max}$ on z_0 follows quite obviously the infinite superlattice from (2), $H_{0\max}(z_0 + \Lambda) = H_{0\max}(z_0)$. As it was shown in [2], the largest value of $H_{0\max}$ corresponds to z_0 which coincides with the center of any S layer. And the smallest value of $H_{0\max}$ corresponds to z_0 which coincides with the center of any N layer. Both z_0 values are solutions of the following equation obtained from the variation principle:

$$z_0 = \frac{\int z \psi^2(z; z_0) dz}{\int \psi^2(z; z_0) dz}, \quad (5)$$

which accounts for the corresponding solution for the wave function (WF), being symmetrical with respect to the middle of S layer or with respect to the middle of N layer. At temperatures close to T_c , due to the "smearing" of WF over the whole sample, the finite dimensions of S/N structure start to be substantial. Consequently, it is necessary to consider only one real symmetry plane (instead of the infinite number of XY symmetry planes in infinite superlattice). Correspondingly instead of the degeneracy of z_0 we obtain from (5) the unique value $z_0=0$, which corresponds to the symmetric WF. At large values of the magnetic field (or for $T < T_{c\alpha} < T_c$), when WF is localized within a single S layer [6], the sample is practically equivalent to an infinite multilayer (the sample boundaries do not influence more WF). In this case the infinite structure symmetries are *re-established* in the samples. Consequently, the curve $H_{c2\parallel}(T)$ for N-type sample approaches the same one for S-type (Fig. 2).

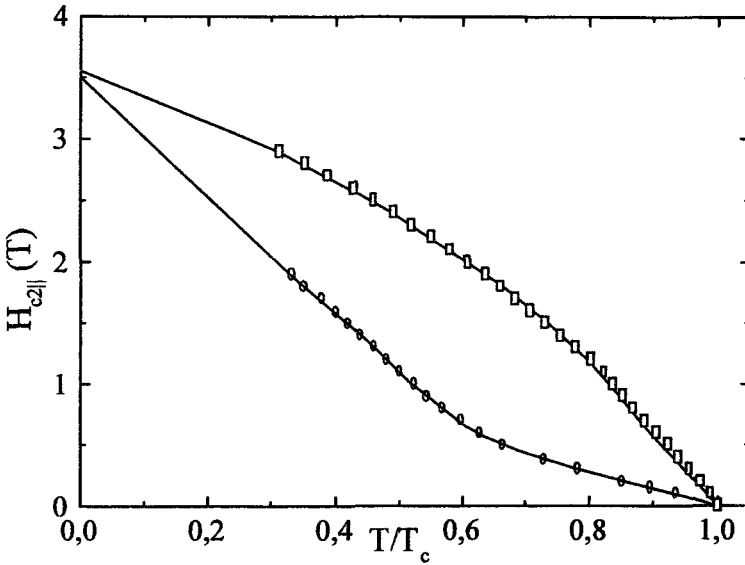


Figure 2. Parallel magnetic fields for samples KS9 (squares) and KN10 (circles) versus T/T_c together with fitting according to the Eqs. (2), (3'), (4), $P=0.3$.

For precise construction of the corresponding $H_{c2\parallel}(T)$ dependence of N-type samples one should solve the self-consistent task (2), (3'), (4), (5). But this procedure presents a large technical problems. That is why we fit the experimental data in the following way. For KS9 (in this case $z_0=0$) Eqs. (2), (3'), (4) were solved numerically. The dependence ξ_{S0} on P was calculated from the value $H_{c2\parallel}(0)$ which was obtained by extrapolating the experimental dependence $H_{c2\parallel}(T)$ to zero temperature. Parameters ξ_{Nc} and P were calculated according to the known T_c value

and to the experimental $H_{c2\parallel}(T)$ values for the intermediate temperatures $0 < T < T_c$. Then, using obtained ξ_{S0} , ξ_{Nc} and P we calculated the curve $H_{c2\parallel}(T)$ for KN10 with z_0 as a parameter of the fit. The results are shown in Fig. 2.

In conclusion, we have fabricated in the same deposition run a couple of Nb/Cu samples with $d_N = d_S \approx 200$ Å only differing in the total number of bilayers. In one sample the symmetry plane was situated at the middle of S layer, while in the other sample it was located in the middle of N layer. The observed $H_{c2\parallel}(T)$ dependencies were different. For the sample with the symmetry plane in the S layer the $H_{c2\parallel}(T)$ shape is square root like up to T_c . For the sample with the symmetry plane in the N layer the $H_{c2\parallel}(T)$ curve is the usual one for a S/N multilayer. This result has been explained taking into account the real symmetry of the system. The effect of the change of the symmetry from the symmetry of the finite structure to the symmetry of the infinite one is an important additional condition for a reasonable choice of the parameters of any model, which describes the superconducting state of S/N nanostructures.

References

1. Gvozdkov V. M., A crossover in the temperature behavior of the perpendicular upper critical magnetic field of layered superconductors and thin films, *Low Temp. Phys.* **25** (1999) pp. 936-947.
2. Kushnir V. N., Petrov A. Yu., Prischepa S. L., Upper critical fields in superconductor-normal metal type superlattices in the Ginzburg-Landau approximation, *Low Temp. Phys.* **25** (1999) pp. 948-652.
3. Mercaldo L. V., Attanasio C., Coccoresc C., Maritato L., Prischepa S. L., Salvato M., Superconducting-critical-temperature oscillations in Nb/CuMn multilayers, *Phys. Rev. B* **53** (1996) pp. 14040-14042.
4. Abrikosov A. A., *Fundamentals of the theory of metals* (Nauka, Moscow, 1987).
5. Jin B. Y., Ketterson J. B., Artificial metallic superlattices, *Adv. Phys.* **38** (1989) pp. 189-336.
6. Takahashi S., Tachiki M., Theory of the upper critical field of superconducting superlattices, *Phys. Rev. B* **33** (1986) pp. 4620-4631.
7. de Gennes P. G., Boundary effects in superconductors, *Rev. Mod. Phys.* **36** (1964) pp. 225-237.

This page is intentionally left blank

CHEMISTRY OF NANOSTRUCTURES

This page is intentionally left blank

INVITED

SELF-ASSEMBLING ALKALI NANOWIRES AT SEMICONDUCTOR SURFACES

MARIA GRAZIA BETTI

*Dipartimento di Fisica Università "La Sapienza"
Piazzale Aldo Moro 5 00185 Roma*

E-mail: betti@roma1.infn.it

Alkali metals deposited on suitable substrates are model systems to investigate the formation of self-assembled metallic nanowires. The aim of this review is to provide a comparative study of the atomic geometry and the mesoscopic properties of self-assembled alkali nanowires. The self-assembling is controlled at the atomic scale via the topography deduced from Scanning Tunnelling Microscopy. The long range ordering of the nanowires can be easily followed by grazing incidence x-ray diffraction proposing a model to study the probability distribution of the nanowires at the surface. Self-assembling of Cs adatoms on III-V(110) surfaces is the result of competing driving forces: a short range attractive force inducing the coupling of Cs adatoms within the chain and a long range dipole-like repulsive interaction keeping the chains apart from each other

1 Introduction

Nanostructures have triggered increasing attention over the last years, due to their fundamental intriguing properties and to the potential application to electronic and optoelectronic technologies. The design of nanoscale devices requires the fabrication of structures with well-controlled architecture at the atomic scale. The search of viable methods of nanostructures assembly is being also pursued with strength because of the unique potential of their physical properties due to the reduced dimensionality (quantum dots, metallic nanowires, etc). Two avenues are being examined in which nanostructures are building up using surface techniques. In one, specific nanostructures are created manipulating individual atoms or molecules with Scanning Tunnelling Microscope (STM) tip. An alternative method is to use templates to pattern overlayer growth. Self-organization on solid surfaces has been recognized as a promising alternative for growing uniform nanostructures with regular size and spacing. Alkali metals adsorbed on suitable substrates are appealing model systems to investigate the formation of metallic nanowires. As a prototype of these systems, Cs deposited on III-V(110) surfaces self-assembly forming chains extending for several hundreds of Ångströms [1-6]. Generally alkali atoms adsorbed on metallic substrates disperse owing to long range repulsion induced by strong dipolar interaction [7,8], while they occupy 1D channel deposited on the (110) surfaces of noble metals in the presence of missing row reconstructed

surfaces [9]. Self-assembling of Cs adatoms on III-V(110) surfaces is the result of competing driving forces: a short range attractive force inducing the coupling of two Cs adatoms and the formation of the chain and a long range dipole-like repulsive interaction keeping the chains far away from each other [6].

Scanning tunnelling microscopy study has brought considerable insight into the local structure of alkali nanowires. The Cs adatoms form very stable linear structures oriented along the [110] direction even at very low coverage. The local structure of Cs nanowires has been followed on GaAs(110), InSb(110), and InAs(110) substrates [1-5]. Total energy calculations to the [-110] direction show a topology of the energy surface with high anisotropic perpendicular barrier parallel to the chain direction favouring migration of the alkali adatoms in the channels between the substrate chains [6]. The origin of the attractive interaction between the adjacent coupled Cs adatoms within each self-assembled nanowire can be due to the presence of non-equivalent adsorption sites that stabilize the formation of the chains, as predicted by very recent theoretical calculations [10].

Scanning tunnelling microscopy is a unique tool to study the topography at the atomic scale of nanostructures, but long-range ordering of the alkali nanowires and the driving forces of self-assembly can be better understood using a diffraction technique. Preliminary electron and surface x-ray diffraction experiments show a long-range ordered ($2 \times n$) symmetry for this chain structure, with n depending on the distance of the alkali nanowires [11]. The self-assembly and the probability distribution of the nanowires arranged on the surface can be followed analysing the diffuse scattering in the diffraction data as will be presented in the following sections.

Nanostructures of metallic systems exhibit interesting electronic properties due to the reduced dimensionality. Alkali metal chains deposited on semiconductor substrate are insulating. Several theoretical approaches were applied to study the electronic structure of alkali metals on III-V(110) surfaces. A simple atomic geometry is generally supposed with a single alkali atom adsorption site close to the substrate cation [12-15]. Electron correlation effects caused by the low alkali metal density (Mott insulator) can be responsible for the insulating behaviour of these systems.

The aim of this review is to provide a comparative structural study of the atomic geometry and the mesoscopic properties of self-assembled alkali nanowires. The self-assembling is controlled at the atomic scale via the topography deduced from STM. The chemical bonding is monitored by means of core level photoemission. The long range ordering of the nanowires can be easily followed by grazing incidence x-ray diffraction proposing a model to study the probability distribution of the nanowires at the surface.

2 Structure of alkali nanowires: local structure and long range ordering

STM images of Cs adatoms deposited on InAs(110) surface show regular one dimensional zig-zag chains in the $[1-10]$ direction, constituted by Cs atom doublets (as shown in Fig. 1(a)), as already observed in other Cs/III-V(110) interfaces [1-5]. Further deposition induces a layer with an ordered local structure constituted by parallel Cs chains 12-18 Å apart from each other (Fig. 1(b)). From the STM topography the alkali chains are commensurate with the substrate periodicity. A single Cs chain displays a periodicity of 8 Å, corresponding to twice the substrate lattice vector, while the spacing d between chains is always a multiple of the InAs surface lattice vector a_1 along $[001]$. The average chain length is already 250 Å at 3 % of the saturation coverage and increases up to 700 Å at about 50 % of the saturation coverage. While for the Cs/GaAs(110) interface a chain fragmentation in small Cs clusters has been observed [2], that interface shows an ordered chain structure until the first layer is formed (about half saturation coverage). The distribution of the Cs chains distances is always far from the exponential distribution typical of a random process. The chains repel each other in the $[001]$ direction even when they are 50 Å apart.

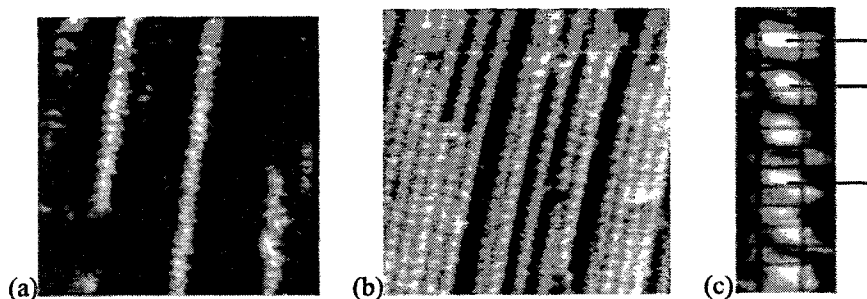


Figure 1. STM images of Cs on InAs(110) at 300 K at different coverages: (a) $\Theta = 0.07 \Theta_s$ (200 Å x 200 Å), (b) $\Theta = 0.35 \Theta_s$ (200 Å x 200 Å), (c) fragment of a Cs chain (12 Å x 60 Å).

Information about the nature of chemical bonding can be deduced from core level photoemission since the core levels are sensitive to the local electric field at the excited atoms as well as to the screening properties of the local electron density.

We have studied the Cs deposited on InAs(110), GaAs(110), GaP(110), InP(110) surfaces by high resolution UV photoemission spectroscopy [16-17]. From Cs 5p and Cs 4d core level photoemission spectra two different spin-orbit split components are clearly resolved during the chain formation as shown in Fig. 2. The two components for the Cs 4d present a relative energy shift of 0.7 eV for InAs(110), 0.9 eV for InP(110), 0.95 eV for GaP(110).

This picture is in agreement with the formation of Cs dimers, formed by two unequivalent Cs atoms. The first Cs atoms is bound to cation atoms (with consistent charge transfer), the other produces electronic level re-hybridization on the

underlying anion and cation as reported in [16]. The non-equivalent adsorption sites are the origin of the attractive interaction between the adjacent coupled Cs adatoms within each self-assembled nanowire. The dimers assemble along the $[1\bar{1}0]$ direction forming the nanowires, as observed in STM. The surface geometry is locally modified, but the relaxed configuration of the topmost layer is preserved in agreement with the theoretical model [10] in the case of Cs/InAs(110) interface. An analogous behavior of the alkali metal core-level components was also observed at the Cs 5p core levels for Cs/InAs(110) interface, and for Cs/GaAs(110) and Cs/GaSb(110) systems [18-20].

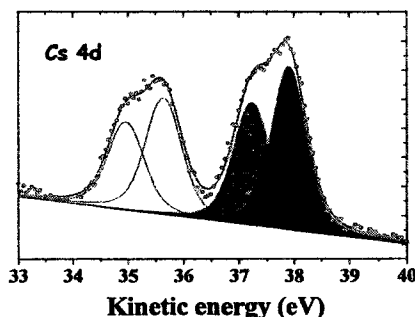


Figure 2. Cs 4d core levels for the Cs/InAs(110) interface. Data is shown along with the results of a fitting procedure through use of Lorentzian-Gaussian spin-orbit split components.

A confirm of the chain distance dependence as a function of coverage can be also inferred analyzing the binding energy shifts of the Cs core level components. A depolarization effect influences the Cs core levels binding energy. The long range repulsion can be driven by a dipole like mutual interaction. In fact we observe a different charge transfer between the adatom and the substrate. The Cs chain can be treated as dipole wires, which interact each other according to a dipole-like repulsive interaction scaling with inverse square of the chain-chain distance as reported in [6]. The self-assembly of the Cs nanowires is therefore driven by two causes: a short range strongly anisotropic attractive force that allow the formation of the nanowire and a long-range dipole like repulsive interaction that tend to keep chains apart.

Preliminary electron and surface x-ray diffraction experiments show a long-range ordered $(2 \times n)$ symmetry for this chain structure, with n depending on the coverage. We have followed step by step, at low Cs coverages, the evolution of one-dimensional (1D) Cs chains with LEED images. In Fig. 3 we report a LEED image at about 0.2Θ and 0.4Θ of the saturation coverage Θ_s . One can clearly observe the integer order sharp spots of the (1×1) cell and the broad extraspot due to the ordering of the Cs chains with a reconstruction $(2 \times n)$. The behaviour of the LEED images indicates how the position and shape of these extraspot shift towards the

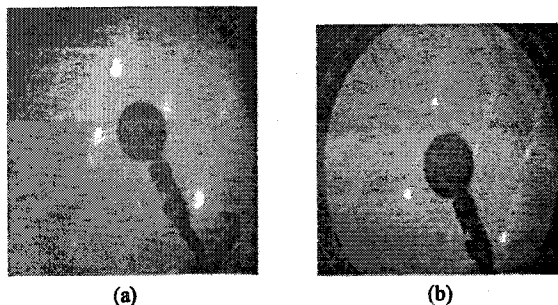


Figure 3. LEED patterns for Cs/InAs(110) (a) $\Theta = 0.3 \Theta_s$, (b) $\Theta = 0.5 \Theta_s$.

middle of the reciprocal cell (coexistence of 2×3 and 2×2 reconstructions) depending on the Cs coverage.

A complete set of grazing incidence X-ray diffraction data has been collected at the DW12 beamline at LURE (Orsay). The data analysis show a structural model reported

in Fig. 4. The proposed atomic geometry confirms the presence of two non equivalent Cs adsorption sites: one Cs atom is on a site along the In dangling bond, with the derelaxation of the In atom of the clean surface (unbuckling site); the second Cs atom of the chain is in a site where the underlying In and As atoms undergo a light buckling increase. This scenario is in good agreement with core level photoemission spectroscopy investigation [16]. The Cs-Cs dimer distance in the chain is about 6.9 Å.

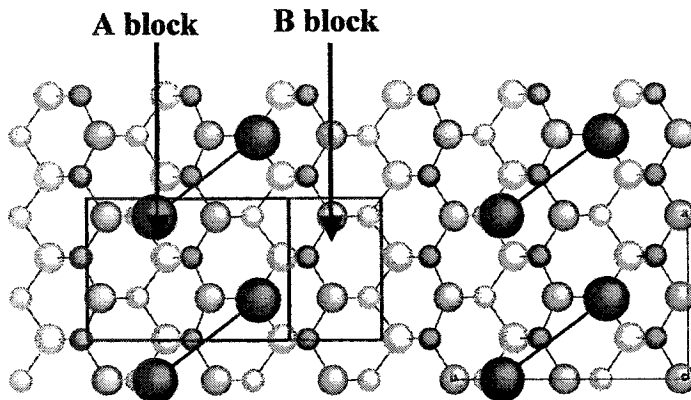


Figure 4. Top view of the (110) plane of the (2×2) reconstruction (A block) alternated with cells of the InAs relaxed surface (B block).

The analysis of the diffuse scattering along the k reciprocal axis (the direction perpendicular to the Cs chains) gives useful information to determine the probability distribution of the nanowires at different Cs coverage. The diffuse scattering distribution can be derived by a theoretical simulation starting from a sequence of situations: A blocks, representing the structural model of the Cs filled 2×2 unit cell, and B blocks, which represent the 1×2 clean relaxed unit cell (see Fig. 4). The

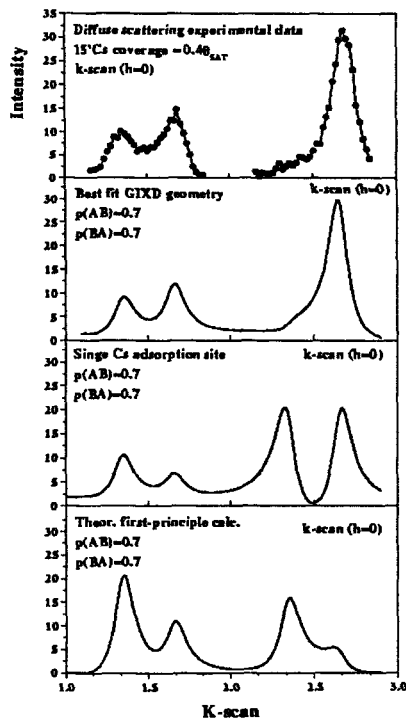


Figure 5. Diffuse scattering experimental data at 0.4 Θ s compared with the theoretical simulations for different structural models: (a) single Cs adsorption site, (b) geometry deduced from [10], (c) geometry obtained from the best fit of the GIXD data.

distance, and 15 % of 24 Å distance. The non random Cs-chain distance distribution is in very good agreement with the STM statistical investigation [6].

3 Conclusions

A comparative study of the structural properties of self-assembled Cs 1D chains is performed by means of microscopy and diffraction techniques. The alkali chains are constituted by adjacent couples of Cs adatoms with different adsorption sites.

The mesoscopic properties of the self-assembled chains show a probability distribution of the chain distances far from the exponential distribution of a random nucleation process. This behaviour has been confirmed following the diffuse scattering evolution and the statistic of the chain distance from the STM images. The chains can be treated as dipole wires which interact with each other according

simulation of the diffuse scattering distribution is a function of 2 probabilities: $p(AB)$, which is the probability of the A block to be followed by the B block, and $p(BA)$, which is the probability of the B block to be followed by the A block. In Fig. 5 we compare the diffuse scattering experimental data at 40 % of saturation coverage, and the theoretical simulations for different structural models proposed: the atomic structure with a single Cs adsorption site, the theoretical approach from first-principle [10] and the model deduced from the best fit of the grazing incidence X-ray diffraction (GIXD) data. The agreement with experimentally derived structural model is really good. Moreover, from the probability parameters derived from the simulation, we can deduce the periodicity of the incommensurate $2\pi n$ phase along the [001] direction. For this particular coverage we derive 66 % of Cs-chains filled surface, and 33 % of clean surface; there is a 30 % of probability to have Cs chains distant 12 Å, 49 % of 18 Å

to a dipole-like repulsive interaction, scaling with the inverse square of the chain-chain distance, keeping chains apart.

4 Acknowledgements

The author wishes to thank Carlo Mariani for the fruitful collaboration throughout the course of this work, Silvio Modesti for STM measurements, and Valdis Corradini, Michèle Sauvage Simkin for the collaboration at LURE synchrotron radiation facility for GIXD results.

References

1. Whitman L. J., Stroscio J. A., Dragoset R. A., Celotta R. J., *Phys. Rev. Lett.* **66** (1991) 1338.
2. First P. N., Dragoset R. A., Stroscio J. A., Celotta R. J., Feenstra R. M., *J. Vac. Sci. Technol. A* **7** (1989) 2868.
3. Whitman L. J., Stroscio J. A., Dragoset R. A., Celotta R. J., *Phys. Rev. B* **44** (1991) 5951.
4. Whitman L. J., Stroscio J. A., Dragoset R. A., Celotta R. J., *J. Vac. Sci. Technol. B* **9** (1991) 770.
5. Modesti S., Falasca A., Polentarutti M., Maria Grazia Betti, De Renzi V., Mariani C., *Surf. Sci.* **447** (2000) 133.
6. For a review, see: *Physics and Chemistry of Alkali Metal Adsorption*, ed. by Bonzel H. P., Bradshaw A. M., Ertl G. (Elsevier, Amsterdam, 1989).
7. Schuster R., Barth J. V., Ertl G., *Surf. Sci.* **247** (1991) L229.
8. Chandravarkar S., Diehl R. D., *Phys. Rev. B* **38** (1988) 12112.
9. Bechstedt F., Scheffler M., *Surf. Sci. Rep.* **18** (1993) 145 and references therein.
10. Calzolari A., Pignedoli C. A., Di Felice R., Bertoni C. M., Catellani A., *Surf. Sci.* **454-456** (2000) 207.
11. Corradini V., Maria Grazia Betti, Sauvage M., to be published.
12. Ortega J., Flores F., *Phys. Rev. Lett.* **63** (1989) 2500; Fong C. Y., Yang L. H., Batra I. P., *Phys. Rev. B* **40** (1989) 6120; Ortega J., Pérez R., García-Vidal F. J., Flores F., *Surf. Sci.* **56-58** (1992) 264.
13. Wang X. W., Chen C., *Phys. Rev. B* **54** (1996) 13436; Chen C., Wang W. W., *J. Phys.: Condens. Matt.* **10** (1998) 731.
14. Hebenstreit J., Heinemann M., Scheffler M., *Phys. Rev. Lett.* **67** (1991) 1031; Hebenstreit J., Scheffler M., *Phys. Rev. B* **92** (1992) 10134.
15. Pankratov O., Scheffler M., *Phys. Rev. Lett.* **71** (1993); *Surf. Sci.* **287/288** (1993) 584.
16. Maria Grazia Betti, Corradini V., Gardonio S., Bertoni G., Mariani C., Gavioli L., Belkou R., Taleb-Ibrahimi A., *Surf. Sci.* (2001).

17. Maria Grazia Betti, Morucci S., Gardonio S., Gavioli L., Belkou R., Taleb-Ibrahimi A., to be published.
18. Faraci G., Pennisi A. R., Gozzo F., La Rosa S., Margaritondo G., *Phys. Rev. B* **53** (1996) 3987.
19. Schirm K. M., Soukiassian P., Mangat P. S., Soonckindt L., *Phys. Rev. B* **49** (1994) 5490.
20. Wong T. M., DiNardo N. J., Heskett D., Plummer E. W., *Phys. Rev. B* **41** (1990) 12342; Mangat P. S., Soukiassian P., *Phys. Rev. B* **52** (1995) 12020.

RELAXATION PROCESSES IN SELF-ASSEMBLED NANOSCALE PHOTOSYNTHETIC MODELS

E. I. ZENKEVICH, A. M. SHULGA

*Institute of Molecular and Atomic Physics
F. Skaryna Ave. 70, 220072 Minsk, Belarus*

E-mail: zenkev@imaph.bas-net.by

C. VON BORCZYKOWSKI

*University of Technology Chemnitz
Reichenhainer Str. 70, 09107 Chemnitz, Germany*

E-mail: borczykowski@physik.tu-chemnitz.de

Our research focuses on the modeling of primary photoevents (electronic excitation energy transfer and photoinduced electron transfer) realized in natural structurally well-organized photosynthetic systems. Nanoscale self-assembling multiporphyrin arrays with well-defined geometry, controllable number and properties of interacting components were formed in solutions and polymeric films using the combination of covalent and non-covalent binding interactions. On the basis of steady-state, time-resolved picosecond fluorescence ($\Delta_{1/2} \approx 30$ ps) and femtosecond pump-probe ($\Delta_{1/2} \approx 280$ fs) spectral-kinetic data at 77-300 K it has been found that the non-radiative relaxation of excited states in these models is due to the competition between the singlet-singlet energy transfer (within < 10 ps) and electron transfer (within 600 fs – 700 ps). The interplay between the above processes depends on the structure, spectral and redox properties of interacting subunits and may be driven by temperature and solvent polarity. The mechanisms of relaxation processes are discussed.

1 Introduction

Within last decade, a great progress has been achieved in the study of overall hierarchical architecture and energy relaxation dynamics of photosynthetic objects *in vivo*. It has resulted in detailed understanding of the pathways and mechanisms of the primary photoevents by which Nature converts solar energy into a stable electrochemical potential. Now it is well documented that the light reactions occur in two energetically and structurally coupled pigment systems. Sun light energy is initially absorbed by light-harvesting pigment-protein antenna complexes and the excitation energy migrates among interacting pigment chromophores directionally, very fast and efficiently to the photochemical reaction center (RC) [1,2]. Then in RC, the energy of excited states is converted into a stable transmembrane charge separation through a sequence of electron transfer reactions [3,4]. Here, the electron transfer (ET) first step from the excited “special pair” (chlorophyll dimer) to the

intermediate acceptor (pheophytin) occurs within 2-5 ps. The subsequent ET second step from pheophytin to quinone (separated by 1.3-1.4 nm) takes place within ~ 200 ps [3]. Native RC is the highly optimized system where small changes of the energy level may cause the essential reduction in efficiency [4]. Nevertheless, the photoinitiated charge separation in RC seems to be activationless being highly effective in frozen rigid objects at 4.2-7 K [3].

In this respect, the preparation of artificial multichlorophyll or multiporphyrin assemblies with functional properties to mimic important features of the energy migration (EM) and ET events [5-7] is one of the most popular tendencies of *supramolecular chemistry and photochemistry* [8,9]. From the other hand, biological systems can provide useful paradigms for electronic and computational devices at the molecular level. Correspondingly, the hope of the future is that multimolecular aggregates of nanometre dimensions can be used in *molecular electronics* to provide the elementary active units of electronic systems with extremely high component density [10]. On the basis of multiporphyrin moieties, various functional molecular nanodevices have recently been developed: optoelectronic gates, photoinduced picosecond molecular switches, fluorescence sensors, photonic wires (see refs. in [11]).

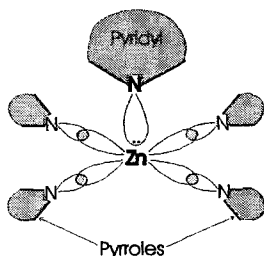


Figure 1. Schematic representation of interaction for N atom of extra-ligand pyridyl ring and central Zn ion of Zn-porphyrin dimer.

using the techniques of organic chemistry. At the second step, newly-prepared molecular blocks may be self-assembled with pyridyl containing porphyrin or chlorin extra-ligands via non-covalent binding interactions (two-fold extra-ligation effect with "key-hole" principle, Fig. 1). It was shown that matching geometry between N atoms in pyridyl containing extra-ligands and Zn-Zn distance in the dimers and trimers plays the essential role in the formation of triads and pentads with relatively well-defined conformational rigidity. The corresponding mutual orientations and intercenter distances could be obtained using optimized structures of the systems (HyperChem software, release 4, methods AM1 and PM3). In the present paper, we discuss EM and ET phenomena in nanoscale multiporphyrin systems of various types and show that these processes determine the main non-radiative relaxation pathways of the locally excited states.

A key feature of our strategy for fabricating highly organized multimolecular tetrapyrrole triads and pentads in solutions and polymeric films is the methodology based on the simultaneous combination of covalent and non-covalent binding interactions [12-15]. At the first step, it includes the design and synthesis of intermediate molecular blocks, such as Zn-porphyrin or Zn-chlorin chemical dimers or trimers linked by spacers of various nature. Additionally, different electron acceptors (quinone, anthraquinone, pyromellitimide, NO₂-group) may be covalently linked to these dimers

2 Methods

Here, we will analyze more closely the results obtained for self-assembled complexes containing covalently linked Zn-octaethylporphyrin dimer with phenyl spacer, (ZnOEP)Ph(ZnOEP), as a basic subunit being the energy and electron donor, *D*. These complexes were formed during a successive titration of the dimer solution with the corresponding extra-ligand. In non-polar solutions (toluene, methylcyclohexane) and rigid polymethylmetacrylate (PMMA) films at 293 K, all triadic and pentadic complexes are characterized by high complexation constants $K_C \sim 10^6\text{--}10^7 \text{ M}^{-1}$ that is by two orders higher with respect to those found for dipyrindinated complexes of the same dimer (ZnOEP)Ph(ZnOEP) [12,13]. High K_C values for triads and pentads reflect the two-point allosteric coordination between two nitrogens of extra-ligand pyridyl rings and two central Zn ions of the dimer.

Steady-state absorption and fluorescence spectra of the complexes have been described in details in our previous papers [12,13]. For the study of EM and ET processes in a real time scale we took advantage of laser kinetic techniques. Fluorescence time-resolved measurements were carried out using laser picosecond fluorescent setup with 2D (wavelength-time) registration based on a dye laser (repetition rate 4 MHz, 10 ps pulses) and a Streak-Scope (the experimental response $\Delta_{1/2} \approx 30$ ps) [14]. Time correlated single photon counting (TCSPC) experiments followed by Global Unlimited software deconvolution were performed for multicomponent kinetic analysis. Pump-probe experiments involved a Coherent MIRA 900 Ti:sapphire laser with a regenerative amplifier and a parametric oscillator running at 1 kHz (of 400–800 nm excitation range $\Delta_{1/2} \approx 280$ fs [16]).

3 Experimental results and discussion

3.1 Photoinduced electron transfer in triads consisting of the dimer (ZnOEP)Ph(ZnOEP) and covalently linked electron acceptors

Among numerous systems of this kind what we have studied it seems reasonable to compare two systems, (ZnOEP)Ph(ZnOEP)-Ph-CH₂-Q (system I, with quinone Q) and (ZnOEP)Ph(ZnOEP)-Ph-CH₂-Pim (system II, with pyromellitimide Pim), having the same structure and spacer but different acceptors *A* (Fig. 2).

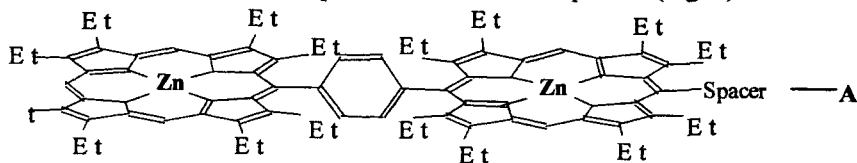


Figure 2. Schematic representation of triads containing the dimer (ZnOEP)Ph(ZnOEP) and electron acceptors *A* of various nature covalently linked in *meso*-position by Spacer.

At 293 K in toluene, two triads with Q and Pim have the same absorption and fluorescence spectra with respect to those for the pure dimer. TCSPC experiments evidently show the strong fluorescence quenching of the dimer: $\tau_s = 34$ ps (system I) and $\tau_s = 135$ ps (system II), while $\tau_{s0} = 1.25$ ns for pure (ZnOEP)Ph(ZnOEP). In addition, it is seen from pump-probe experiments that for the system II new absorption band at ~ 715 nm appears with delay time of ~ 50 ps after the exciting pulse (Fig. 3) belonging to Pim^- radical [18]. Simultaneously a weaker absorption at ~ 670 nm is detected, that corresponds to Zn-dimer^+ radical. Therefore the intracomplex charge separation giving $\text{Zn-dimer}^+ \cdot A^-$ seems to be a major additional non-radiative decaying route of S_1 -states in two triads.

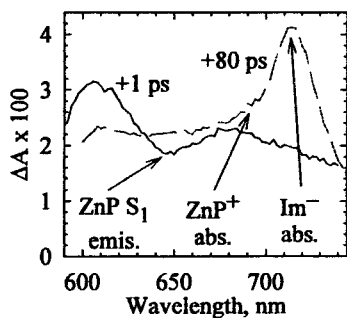


Figure 3. Time-resolved transient absorption spectra of the triad (ZnOEP)Ph(ZnOEP)-Ph-CH₂-Pim in toluene at 293 K at various delays with respect to exciting pulse at 400 nm.

It follows from the ET theory [17] that at ambient temperatures the rate constant k_{ET}^s for endergonic non-adiabatic electron transfer occurring in the “normal” region depends on the redox properties of D and A , the nature and electronic properties of the spacer as well as on the medium polarity. Thus, in the triad with Q ($r_{DA} = 1.08$ nm, free Gibbs energy $\Delta G^0 = E(IP) - E(S_1) = -0.65$ eV) photoinduced ET has to be faster than that for the same triad with Pim ($r_{DA} = 1.3$ nm, $\Delta G^0 = -0.29$ eV). It follows from kinetic data, redox properties and structural parameters of the systems I and II that ET from the dimer to both A 's is described by Marcus theory with the electronic coupling term of $V < 180$ cm⁻¹.

For the diad (ZnOEP)-Ph-CH₂-Q ET is faster ($t_{ET} = 3.7$ ps) than ET for the triad (ZnOEP)Ph(ZnOEP)-Ph-CH₂-Q at the same conditions. In the later case, one has to take into account the role of EM between porphyrin macrocycles in the dimer. Using inductive-resonance model [19], spectral-fluorescent parameters of the pyridinated dimer (ZnOEP)Ph(ZnOEP) [12] ($\tau_s = 1.15$ ns, $\phi_s = 0.012$), the intercenter distance $r_{Zn-Zn} = 1.25$ nm and the orientational factor $k^2 = [\text{Cos}(\mu_D, \mu_A) - 3\text{Cos}(\mu_D, r_{DA}) \cdot \text{Cos}(\mu_A, r_{DA})]^2 = 1.002$ for interacting dipoles, we calculated spectral overlap $J = \int_0^\infty f_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4} = 3.95 \cdot 10^{-14}$ cm⁻⁶M⁻¹ and critical EM distance

$R_0^{\text{theor}} = 2.16$ nm. Correspondingly, EM process between porphyrin macrocycles realizes within $t_{EM} = \tau_s(r_{DA}/R_0^{\text{theor}})^6 = 47$ ps. Therefore $t_{EM} > t_{ET}$ in the triad (ZnOEP)Ph(ZnOEP)-Ph-CH₂-Q. It leads to the decrease of ET efficiency in the triad in comparison with that for the diad (ZnOEP)-Ph-CH₂-Q with the same A .

3.2 Energy migration and electron transfer between π -conjugated macrocycles in porphyrin triads

In photosynthetic reaction centers, the initial photoinduced ET step takes place from chlorophyll "special pair" to pheophytin [3,4], that is between large π -conjugated tetrapyrrole molecules. Such a process is characterized by small reorganization energy λ and small inverse temperature dependence. In this respect, self-assembled porphyrin triads of variable but controllable geometry (Fig. 4) present themselves appropriate models for the study of ET competing with EM when both processes are thermodynamically allowed.

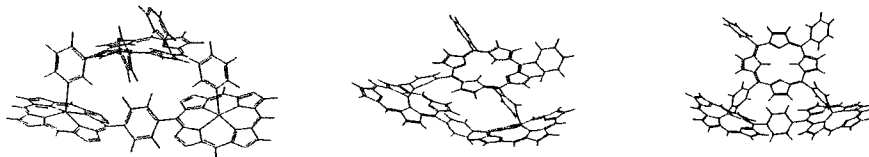


Figure 4. Optimized structures of the two-fold coordinated triad (ZnOEP)Ph(ZnOEP)⊗H₂P with various arrangement of the extra-ligand, dipyridyl containing porphyrin free base H₂P.

In toluene and PMMA films at 293 K, the strong fluorescence quenching of Zn-dimer is observed for all triads. Femtosecond pump-probe measurements indicate that the non-radiative relaxation of the dimer S₁-state in the triads takes place within 1.7±0.1 ps [16]. Fluorescence excitation spectra of the triads evidently show the existence of the dissipative S-S EM Zn-dimer→H₂P (the efficiency Φ = 70-80 % in toluene, EM rate constants $k_{EM}^{theor} = 6.7 \cdot 10^{10} \div 7.5 \cdot 10^{10} \text{ s}^{-1}$). Upon the solvent polarity increase fluorescence excitation spectra for the triads are transformed in to those for the extra-ligand only (e.g. the sensitization effect disappears) while the dimer fluorescence remains strongly quenched. Generally speaking, it means that the photoinduced ET Zn-dimer^{*}...H₂P→Zn-dimer⁺...H₂P⁻ caused by the solvent repolarization becomes dominant with respect to EM. Moreover, TCSPC results reveal that the extra-ligand H₂P fluorescence lifetime is shorten down to 6.2-7.7 ns in the triads in nonpolar toluene even with respect to $\tau_s = 9.3$ -10.0 ns for individual extra-ligands (Fig. 5). This lifetime shortening does not significantly depend on the mutual spatial arrangement of the triad subunits (Fig. 4) but increases upon the solvent polarity rise and/or the temperature lowering.

Recently, we have shown [20] that for the triads under consideration the dynamics of the excited states $|1\rangle = |Zn-dimer^* - H_2P\rangle$, $|2\rangle = |Zn-dimer^+ - H_2P^- \rangle$ and $|3\rangle = |Zn-dimer - H_2P^* \rangle$ may be appropriately described on the basis of the

generalized Haken-Strobl-Reineker theory. In this case, the equation of motion for the relevant reduced density matrix $\sigma_{\kappa\lambda}$ with neglecting of the vibrational substructure of the electronic states may be written in the form

$$\begin{aligned} \frac{\partial}{\partial t} \sigma_{\kappa\lambda} = & -\frac{i}{\hbar} [H_S, \sigma]_{\kappa\lambda} + 2\delta_{\kappa\lambda} \left\{ \Gamma_{\mu\kappa} [n(\omega_{\mu\kappa}) + 1] + \Gamma_{\kappa\mu} n(\omega_{\kappa\mu}) \right\} \sigma_{\mu\mu} \\ & - \sum_{\mu} \left\{ \Gamma_{\mu\kappa} [n(\omega_{\mu\kappa}) + 1] + \Gamma_{\kappa\mu} n(\omega_{\kappa\mu}) + \Gamma_{\mu\lambda} [n(\omega_{\mu\lambda}) + 1] + \Gamma_{\lambda\mu} n(\omega_{\lambda\mu}) \right\} \sigma_{\kappa\lambda} \\ & + \left\{ \Gamma_{\lambda\kappa} [2n(\omega_{\lambda\kappa}) + 1] + \Gamma_{\kappa\lambda} [2n(\omega_{\kappa\lambda}) + 1] \right\} \sigma_{\lambda\kappa}. \end{aligned}$$

Here, the triad Hamiltonian H_S includes the energies E_λ of the corresponding states and couplings between them, $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ denotes Bose-Einstein distribution, $\Gamma_{\kappa\lambda}$ is the damping constant, and $\kappa, \lambda, \mu = 1, 2, 3$. The energies $E_1 = 2.1$ eV, $E_3 = 1.91$ eV and $E_2 = 1.90$ eV (charge transfer state, CT) were taken from our previous paper [16]. The corresponding coherent and dissipative couplings were estimated from literature data. For each parameter set the relevant reduced density matrix $\sigma_{\kappa\lambda}(t)$ has been numerically calculated.

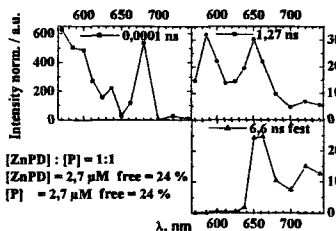


Figure 5. Fluorescence TCSPC amplitude spectra for the triad ($\lambda_{ex} = 545$ nm, toluene, 293 K).

between close lying CT and extra-ligand locally excited S_1 -states. On the basis of these results it may be concluded that in the presence of acetone (5-15 vol %) the increase of temperature induces the crossover from the coherent to the incoherent type of the quantum particle transport.

3.3 Low-temperature electron transfer between porphyrinic subunits in triads (ZnOEP)Ph(ZnOEP)@H₂PF

ET processes in many biological systems appear to be operative at cryogenic temperatures. Nevertheless, most of the porphyrin- and chlorophyll-based *D-A* systems do not undergo effective photoinitiated ET in low-temperature solids due to the destabilization of the ion pair state as compared to the case with polar liquid surroundings at 293 K. In this respect, we have systematically examined self-assembled complexes at 293-77 K and found some models with the effective charge separation at 77-60 K. One of them based on the Zn-dimer (*D*) and a dipentafluorinated porphyrin extra-ligand H₂PF (*A*) is presented in Fig. 6. For this triad in methylcyclohexane at 293 K, the strong fluorescence quenching of both

Such an approach provides the quantitative description of the excitation relaxation in triads caused by the competition between S-S EM and photoinduced ET processes. For instance, calculated dependencies of the extra-ligand H₂P S_1 -state population on the solvent temperature and polarity are in a reasonable agreement with steady-state and kinetic experimental data.

The quenching of H₂P S_1 -state is due to the hole transfer from the extra-ligand to the Zn-dimer being weakened by thermal exchange

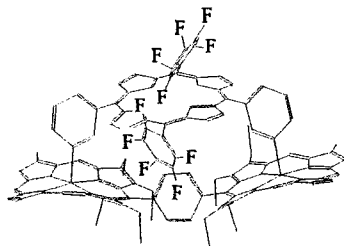


Figure 6. Computer-simulated structure of the triad with di-pentafluorinated extra-ligand.

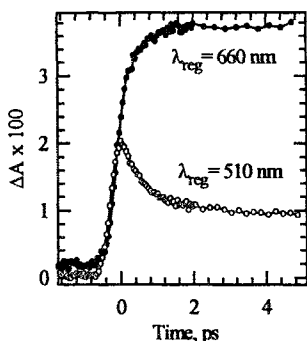


Figure 7. Femtosecond transient absorption kinetics of the triad (ZnOEP)Ph(ZnOEP)⊗H₂PF ($\lambda_{\text{exc}} = 555$ nm, methylcyclohexane, 293 K).

excited triplet T_1 -state of H₂PF via intersystem crossing is not realized. In this case, the effective formation of H₂PF low lying T_1 -state ($\tau_T = 6.4$ μ s in degassed solution) takes place from the upper-lying triplet or singlet radical ion pair states.

3.4 Electron transfer in tetrads via "superexchange" mechanism

One of the key questions in the study of the biologically important long-range ET in *D-bridge-A* systems is the nature of the transfer process. It could be either a sequential (incoherent) hopping between adjacent sites or a direct quantum tunneling (superexchange) between *D* and *A* [21]. With this in mind, we present our results on picosecond TCSPC in tetrads with covalently linked *A*'s of the various nature (Fig. 8). In both tetrads containing Q or Pim the effective fluorescence quenching of the dimer (ZnOEP)Ph(ZnOEP) ($\tau_S < 3$ ps) is due to two reasons: i) S-S EM (ZnOEP)Ph(ZnOEP)^{*}→H₂P ($R_0 = 1.6$ -1.7 nm, $k_{\text{EM}} \approx (2\div3) \cdot 10^{11}$ s⁻¹) and ii) photoinduced ET from the dimer to Q ($r_{\text{DA}} = 1.08$ nm, $\Delta G^0 = -0.65$ eV,

(ZnOEP)Ph(ZnOEP) dimer and H₂PF extra-ligand is due to the photoinduced ET presumably ($\Delta G^0 \approx -0.25$ eV, $r_{\text{DA}} \approx 0.92$ nm). No fluorescence is sensitized via the dimer absorption, and correspondingly S-S energy migration (ZnOEP)Ph(ZnOEP)^{*}→H₂PF is not realized at 293 K. Femtosecond pump-probe results evidently show the increased bleaching of H₂PF at 510 nm attributed to the production of H₂PF⁻ radical anion (Fig. 7). The dynamics of this effective ET step is characterized by a time constant of 700 ± 200 fs. At 120-77 K ET remains still effective (rate constant $k_{\text{ET}} \sim 10^{11}$ s⁻¹) and competes with the singlet-singlet EM (ZnOEP)Ph(ZnOEP)^{*}→H₂PF. There are some reasons for low-temperature ET in this triad: i) fluorinated H₂PF is strongly electron withdrawing and stabilize a negative charge on the H₂PF macrocycle; ii) the coordination of the electron-donating pyridyl rings helps to stabilize a positive charge on the Zn-dimer and thus lowers the energy of the radical ion pair state Zn-dimer⁺...H₂PF⁻. In the triad, ET is adiabatic at room temperature, while at 77 K in rigid solution the electron quantum tunneling may take place. Because of fast ET in the triad the direct population of the locally

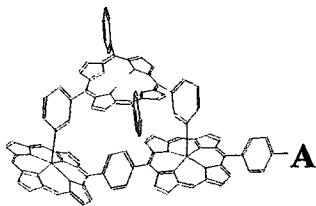


Figure 8. Optimized structure of the triad with covalently linked acceptors *A* ($\text{CH}_2\text{-Q}$ or $\text{CH}_2\text{-Pim}$).

$k_{\text{ET}} = 3 \cdot 10^{11} \text{ s}^{-1}$) or Pim ($r_{\text{DA}} = 1.3 \text{ nm}$, $\Delta G^0 = -0.29 \text{ eV}$, $k_{\text{ET}} = 2 \cdot 10^{11} \text{ s}^{-1}$). In addition, the fluorescence lifetime shortening is observed for extra-ligands in the tetrads with respect to those for individual monomers. In toluene at 293 K, $\tau_{\text{S}} = 970\text{--}1280 \text{ ps}$ for H_2P 's depending on their arrangement in tetrads while for pure extra-ligands $\tau_{\text{S}0} = 9.3\text{--}10 \text{ ns}$. With other extra-ligands, $\tau_{\text{S}} = 1080 \text{ ps}$ and $\tau_{\text{S}0} = 8.3 \text{ ns}$ for chlorin Ch, while fluorescence quenching for THP is absent: $\tau_{\text{S}0} = 4.5 \text{ ns}$.

These facts are explained in terms of photoinduced ET via the “superexchange” mechanism where a “spectator” CT state of the triad, $\text{H}_2\text{P}^+ \text{-(Zn-dimer)}^- \text{-Q}$, mediates the direct ET from the extra-ligand to a distant ($R \approx 1.8\text{--}2.1 \text{ nm}$) *A* (Q or Pim) resulting in an effective transfer rate. In this case the only role of the bridge (Zn-dimer) is to provide virtual orbitals that determine the effective *DA* coupling. The same tendency is observed for the triad with Pim: $\tau_{\text{S}} = 2.67 \text{ ns}$ for H_2P ($\tau_{\text{S}0} = 9.5 \text{ ns}$) however this ET from H_2P to the weaker *A* (Pim) is essentially slower.

4 Conclusions

With a view to better understanding the possible mechanisms of the initial photoprocesses in photosynthetic systems *in vivo*, the excited state dynamics have been comparatively studied for a series of conformationally restricted synthetic nanoscale multiporphyrin arrays in solutions, films and polymeric matrices. For the systems of various complexity it was shown that the high effective EM and/or charge transfer are the main non-radiative relaxation processes. The competition between them is governed by the temperature and solvent polarity. The realization in the artificial systems of a long-distant “superexchange” ET, the low-temperature behavior, and the formation of a triplet state by charge recombination are phenomena heretofore observed presumably in natural photosynthetic objects.

The first results obtained for some triads with electron acceptor show that the photoinduced electron transfer takes place in femtosecond time scale in rigid polymeric films and remains still effective at 77 K. The temperature stability of such systems in films is higher with respect to that for solutions. These properties make the systems to be perspective for the solid phase charge separation.

5 Acknowledgements

This work was supported by the National Foundation for Basic Research of Belarus (Grant Nr.Ph 99-104). The support from Deutscher Akademischer Austauschdienst (DAAD) (2000 Grant, Referat 325) for E.I.Z. is gratefully acknowledged.

References

1. Hu X., Damjanovic A., Ritz T., Shulten K., Architecture and mechanisms of the light-harvesting apparatus of purple bacteria, *Proc. Natl. Acad. Sci. USA* **95** (1998) pp. 5935-5941.
2. Sundstrom V., Pullerits T., van Grondelle R., Photosynthetic light-harvesting: reconciling dynamics and structure of purple bacterial LH2 reveals function of photosynthetic unit, *J. Phys. Chem.* **103** (1999) pp. 2327-2346.
3. Greenfield S. R., Seibert M., Wasielewski M., Time-resolved absorption changes of the pheophytin Q_x band in isolated photosystem II reaction centers at 7 K: energy transfer and charge separation, *J. Phys. Chem.* **103** (1999) pp. 8364-8374.
4. Sporlein S., Zinth W., Meyer M., Scheer H., Wachveitl J., Primary electron transfer in modified bacterial reaction centers: optimization of the first events in photosynthesis, *Chem. Phys. Lett.* **322** (2000) pp. 454-464.
5. Oksanen J. A. I., Zenkevich E. I., Knyukshto V. N., Pakalnis S., Hynninen P. H., Korppi-Tommola J. E. I., Aggregation of Chl a cross-linked by dioxane in aliphatic hydrocarbon solvent 3-methylpentane, *Biochimica Biophysica Acta / Bioenergetics* **1321** (1997) pp. 165-178.
6. Steinberg-Yfrach G., Rigaud J.-L., Moore A. L., Gust D., Moore T. A., Light-driven production of ATP catalyzed by FOF1-ATP synthase in artificial photosynthetic membrane, *Nature* **392** (1998) pp. 479-482.
7. Levanon H., Galili T., Regev A., Wiederrecht G. P., Swec W. A., Wasielewski M., Determination of the energy levels of radical pairs states in photosynthetic models oriented in liquid crystals using time-resolved electron paramagnetic resonance, *J. Am. Chem. Soc.* **120** (1998) pp. 6366-6371.
8. Balzani V., Scandola F., *Supramolecular Photochemistry* (Ellis Horwood, New York, 1991) pp. 53-394.
9. Lehn J.-M., Perspectives in supramolecular chemistry – from molecular recognition towards molecular information processing and self-organization, *Angew. Chem. Int. Ed. Engl.* **29** (1990) pp. 1304-1319.
10. Bloor D., Molecular electronics: science and technology for today and tomorrow. In *An Introduction To Molecular Electronics*, ed. by Petty M. C., Bryce M. R., Bloor D. (Edward Arnold, a division of Hodder Headline PLC, London, 1995) pp. 1-28.
11. Fan J., Whiteford J. A., Olenyuk B., Levin M. D., Stang P. J., Fleischer E. B., Self-assembly of porphyrin arrays via coordination to transition metal

- bisphosphine complexes and the unique spectral properties of the product metallacyclic ensembles, *J. Am. Chem. Soc.* **121** (1999) pp. 2741-2752.
12. Chernook A. V., Shulga A. M., Zenkevich E. I., Rempel U., von Borczyskowski Ch., Complexation and interchromophoric interactions in self-organized porphyrin and chlorin triads, *J. Phys. Chem.* **100** (1996) pp. 1918-1926.
 13. Chernook A. V., Rempel U., von Borczyskowski Ch., Zenkevich E. I., Shulga A. M., Formation and optical properties of self-organized pentameric porphyrin arrays, *Chem. Phys. Lett.* **254** (1996) pp. 229-241.
 14. Zenkevich E. I., Shulga A. M., Bachilo S. M., Rempel U., von Richthofen J., von Borczyskowski Ch., Energy and charge transfer dynamics in self-organized multimolecular arrays. *J. Luminesc.* **77/78** (1998) pp. 354-358.
 15. Knyukshto V., Zenkevich E., Sagun E., Shulga A., Bachilo S. Unusual pathways of triplet state dynamic relaxation in meso-arylsubstituted porphyrins and their dimers at 295 K, *J. Fluorescence* **10** (2000) pp. 55-68.
 16. Bachilo S., Willert A., Rempel U., Shulga A. M., Zenkevich E. I., von Borczyskowski Ch., Efficient low temperature charge transfer in self-assembled porphyrin aggregate. *J. Photochem. Photobiol. A: Chem.* **126** (1999) pp. 99-112.
 17. Kavarnos G. J., *Fundamentals of Photoinduced Electron Transfer* (VCH Publishers, Inc. New York, 1993) pp. 1-342.
 18. Osuka A., Marumo S., Mataga N., Taniguchi S., Okada T., Yamazaki I., Nishimura Y., Ohno T., Nozaki K., A stepwise electron transfer relay mimicking the primary charge separation in bacterial photosynthetic reaction center, *J. Am. Chem. Soc.* **118** (1996) pp. 155-168.
 19. Zenkevich E. I., Shulga A. M., Chernook A. V., Sagun E. I., Gurinovich G. P., Dipole-dipole and exchange energy transfer in different types of porphyrin chemical dimers, *Proc. of Indian Acad. Sci., Chem. Sci.* **107** (1995) pp. 795-802.
 20. Zenkevich E. I., Kilin D. S., Willert A., Bachilo S. M., Shulga A. M., Rempel U., von Borczyskowski C., Photoinduced electron transfer dynamics for self-assembled porphyrin arrays in solutions and films, *Mol. Cryst. Liq. Cryst.* **362** (2001) (in press).
 21. Kuhn O., Rupasov V., Mukamel S., Effective bridge spectral density for long-range biological energy and charge transfer, *J. Chem. Phys.* **104** (1996) pp. 5821-5828.

ELECTRONIC PROCESSES IN NANOCOMPOSITE FILMS

R. D. FEDOROVICH, O. E. KIYAYEV, A. G. NAUMOVETS, P. M. TOMCHUK

*Institute of Physics, National Academy of Sciences of Ukraine
46 Prospect Nauki, UA-03028, Kiev 28, Ukraine*

E-mail: naumov@iop.kiev.ua

A brief review of some approaches which can be used to govern the conduction as well as electron and light emission properties of island metal films on dielectric substrates is given. Two approaches are considered: (1) the control of the film structure by evaporation of metal onto grooved substrates, which allows preparation of chain island films, and (2) evaporation of organic molecules onto the island films that results in formation of planar metal-organic nanocomposites. Some peculiar properties of these systems such as voltage-controlled negative differential resistance and electroluminescence are described and discussed.

1 Introduction

Investigations of island metal films (IMFs) on dielectric substrates have revealed a number of substantial differences between their properties and properties of continuous thin metal films [1-4]. In particular, the passage of electric current through any IMF can generate electron and light emission from it, which is thermally nonequilibrium in nature. A prerequisite for the observation of these phenomena is usually the formation of stable percolative current channels in the film, which can readily be attained by a procedure termed electroforming. In this procedure, one applies a voltage to the film that is sufficient to induce its structural rearrangement, probably due to intense electromigration. The greater part of a current channel represents a nanodispersed film in which both the size of islands and the distance between them are in the range of a few nanometers. There are also some relatively large islands (200-400 nm in diameter) which lie rather far apart.

The electroforming results in the appearance of a new quality of the film: its capability to emit electrons and light at voltages which are several times lower than those used in electroforming [1,4]. Normally, the conduction current-voltage characteristic of an IMF is linear (Ohmic) at low voltages and becomes superlinear at higher voltages (Fig. 1). In a typical geometry when the distance between the contacts is 5-10 μm , the transition to the non-Ohmic behavior starts at voltages which can be as low as a few Volts. It is just the voltage region where the electron and light emission from the film sets in. The emission characteristics, under optimum operating conditions, remain reasonably stable over the time as long as 10^3 - 10^4 h.

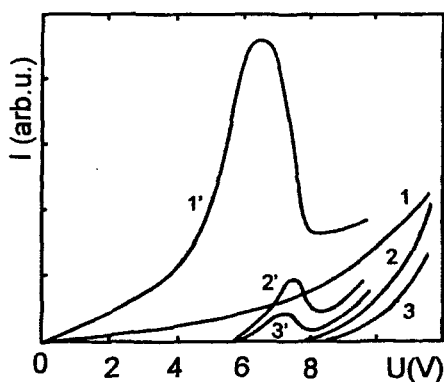


Figure 1. Voltage dependences of the conduction current I_c (1), electron emission current I_e (2) and light emission intensity I_{ph} (3) for the island film prepared on a flat substrate. (1')–(3') the same dependences for the film covered with an organic overlayer (schematically).

The most consistent interpretation of the electron and light emission from IMFs is based on the concept of nonequilibrium heating of the electron gas in nanoparticles which are energized either by passing a current through the IMF or by its exposure to an infrared laser beam [2–4].

An important task is search for the ways of control and modification of IMF properties. This is the subject of the present paper, in which we focus on conduction current characteristics and light emission from IMFs. The electron emission from IMFs has been discussed in detail in our recent reviews [3,4].

2 Chain island films

One of the obvious possibilities for the film properties control is to govern the film structure. The structure should be controlled over an area of 10^{-4} – 10^{-2} cm², which is a typical area of IMF emitters. To this end, in addition to the use of appropriate evaporation regimes of self-organization of the islands [5], one can exploit the impact of substrate relief upon the film structure. If the island film is deposited by vacuum metal evaporation onto a flat substrate prepared by conventional methods (a polished glass or quartz plate mica, etc.), the islands and the current channels are distributed rather randomly over the surface. This is caused by the disordered positions of various surface defects, which are sites of the island nucleation.

However, if the film is prepared by grazing-angle evaporation of a metal onto a grooved substrate, its properties become more controllable [6]. The grooves can be made mechanically, with the aid of photolithography and other techniques. We used

The electron and light emission stems from submicron-sized spots located within the current channels and named emission centers. Such a center occupies the whole (also submicron) width of the current channel, but only a small part of its length spanning the gap between the contacts. The density of nanoislands within the emission center is reduced, which causes an enhanced voltage drop in this region. Usually this occurs around a large island and, as a rule, a current channel contains only one emission center. It should be stressed that the emission properties depend mainly on the processes that occur within the emission centers.

substrates with parallel grooves spaced $\approx 1.6 \mu\text{m}$ apart. In this case the film consists of nearly parallel island chains filling the grooves. The chains represent, in fact, a kind of "prefabricated" current channels so the special electroforming procedure proves unnecessary: the electron and light emission is recorded immediately on applying the operating voltage to such a film. As will be shown below, the chain island films possess also other feature.

3 Modification of IMF properties by organic overlayers

Another possibility to modify properties of IMFs is to cover the islands with various overlayers and/or fill the gaps between them with a suitable substance. In the latter case one actually obtains a planar composite system in which the material deposited between the islands, together with the islands themselves, plays an active part in governing the properties of this system.

It has long been known that evaporation of barium oxide and other electropositive adsorbates, which effectively reduce the work function, results in strong enhancement of the electron emission from IMFs [4,7]. However, the shape of the current-voltage characteristics of both conduction and emission current remains in this case qualitatively the same.

Much more varied modification of IMF properties is attainable with organic overlayers (for the history of these studies, see reviews [4,8] and references therein). Fig. 2 shows a current-voltage characteristic recorded after deposition of a few monomolecular layers of naphthalene (C_{10}H_8) onto a gold IMF. The most remarkable feature is its N-type shape indicating voltage-controlled negative differential resistance (VCNR). Qualitatively similar effects have been observed after evaporation of other organic adsorbates, such as stearone [$(\text{C}_{17}\text{H}_{35})_2\text{CO}$], benzene (C_6H_6), xylene [$\text{C}_6\text{H}_4(\text{CH}_3)_2$]. In all the cases the evaporation was carried out onto IMFs with formed current channels and emission centers. This is a prerequisite for the observation of VCNR, which testifies that the processes occurring within the emission centers are decisive for VCNR.

It is also important to emphasize that emergence of VCNR is strongly aided if the deposition of organic molecules is carried out in the presence of a voltage applied to the film. This observation suggests that a significant role belongs to polarization of evaporated organic molecules by electric field ($\sim 10^4$ - 10^5 V/cm) existing between the islands and to their pulling into the inter-island gaps where the field is the highest. The result seems to be a self-assembly of the molecules into bridges, which span the gaps and, together with the metal islands, combine into a nanocomposite. It should be recalled that the possibility of the formation of molecular complexes through alignment of polarized molecules in the high electric field created near the surface of metal tips was discussed long ago [9]. In the case of long molecules, such as e.g. stearone whose molecule is $\approx 5 \text{ nm}$ long, one molecule can span the whole inter-island gap. The structure obtained in this situation, may be

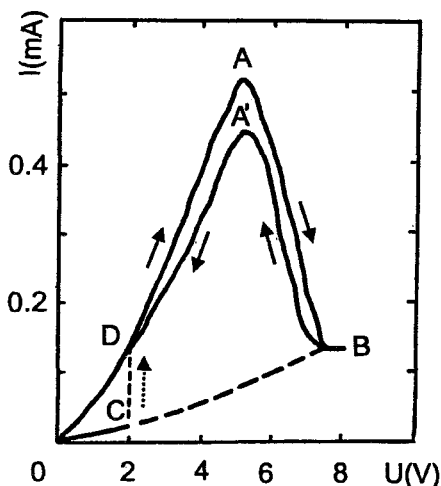


Figure 2. Conduction current-voltage curves of Au island film covered with a naphthalene overlayer. $T=300$ K. ODA: low-resistance state; BCO: high-resistance state obtained at fast voltage reduction; BA'O: the same at slow voltage reduction; OC: region of field memory in the high-resistance state; CD: switching to the low-resistance state at the threshold voltage.

similar to molecular monolayers self-assembled in a molecular electronic device described recently by Chen et al. [10]. In the case of small-sized molecules such as benzene, xylene and naphthalene, a larger number of molecules may be needed to form the nanometer bridges between the islands. Whether the structure of such bridges is amorphous, crystalline or consists of some molecular filaments, remains unclear at present.

The shape of the current-voltage curves with VCNR was only weakly dependent on the chemical nature of evaporated organic materials listed above. At the same time, it depends critically on the number of the current channels, their characteristics and disposition between the contacts.

Let us now consider the main regularities of the behavior typical for IMFs with negative differential resistance.

(1) The VCNR section in the conduction current-voltage curve disappears after the annealing of the film at $300-400^{\circ}\text{C}$, which causes desorption of the organic overlayer. However, if the film is again covered with organics at room temperature, the VCNR is restored. This cycle can be reproducibly repeated many times. These observations indicate that the presence of organic layers is crucial for VCNR in IMFs.

(2) The cooling of IMFs which are in the high-resistance state down to 100 K or below inhibits the VCNR behavior. However, the VCNR is restored when the temperature is raised up to $120-130$ K. For IMF samples which were in the low-resistance state, lowering of the temperature down to 100 K results in the following effect: the sample, on passing once to the high-resistance state, remains in it indefinitely long. These findings show that some thermally activated processes are also essential for the transition from the high-resistance to the low-resistance state. It is also interesting to note the difference in the thermal resistance coefficients for the high-resistance and low-resistance states. In the former case this coefficient, measured in the temperature range $20-300$ K, is negative as for clean IMFs and semiconductors. In the low-resistance state it is similar to that of metals.

(3) The downward leg of the current-voltage curve is sluggish with the characteristic time of the order of a few seconds. If the downward voltage sweep is slow in comparison with this time (say, the sweep time is ~ 1 min), the return trace of the current almost coincides with its direct trace (Fig. 2, section BA'O). On the other hand, if the downward voltage sweep is fast enough (≤ 0.1 s), the conduction current varies along the high-resistance branch of a rather wide hysteresis loop (Fig. 2, section BCO). The high-resistance state is conserved indefinitely long in the interval 0-2 V (section OC), i.e. the film has a property of field memory. However, the voltages above a threshold (equal to ≈ 2 V in Fig. 2) restore the low-resistance branch (section CD).

(4) The resistances in the high- and low-resistance states differ usually only several times for IMFs deposited on flat substrates. For the films prepared on grooved substrates, the ratio of the resistances can be $\geq 10^3$ and the transition occurs almost jumpwise, i.e. one has actually a regime of sharp switching. The transition from low-resistance to high-resistance state occurs in a time $\leq 1 \mu\text{s}$ and the backward transition lasts for ~ 1 s. Such films were found to provide at least 5×10^4 stable switching cycles.

(5) To elucidate more reliably the processes underlying the VCNR and other peculiar properties of IMFs, it is desirable to experiment with films having only one emission center. Such situation was attained in the geometry where one of the contacts to the film represented a metal tip and another was a usual "wide" contact. The gap between the contacts on the substrate was about $1 \mu\text{m}$. This geometry allowed preparation of a film containing only one emission center, which was detected by its luminescence in the red-orange spectral region.

Fig. 3 shows the conduction current-voltage curve with a sharp switching obtained for Al film covered with an organic overlayer. It should be recalled that existing models of the threshold switching elaborated for semiconductors consider thermal and electronic mechanisms as well as a combined electrothermal mechanism, which is accepted as the most general and realistic [11]. In the case of organic inter-island bridges, thermal effects can inflict destruction (in particular, desorption) of the bridges. The bridges can be restored at lower voltages (and temperatures) by diffusion of organic molecules to the emission centers from adjacent film regions. The electronic processes can lead to formation of the space charge by filling localized electronic levels. It cannot be ruled out, however, that processes in single organic molecules, which reflect their specific electronic structure, may essentially determine switching in molecular nanobridges [10]. We intend to discuss this possibility on the basis of a broader set of data in a separate paper.

(6) Fig. 4 presents a current-voltage characteristic of a stearon-covered gold IMF as well as the dependence of the luminescence intensity on voltage in the VCNR region. The luminescence intensity varies as the absolute value of the derivative of the conduction current, i.e. it is closely related to charge redistribution within the IMF. The mechanisms of electroluminescence in organic solids are at

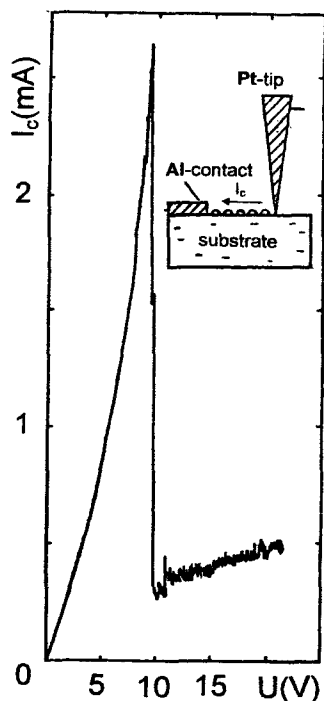


Figure 3. Switching of the conduction current in Al island film covered with a mixture of aliphatic compounds and having one emission center at 300 K. The geometry of experiment is shown in the inset.

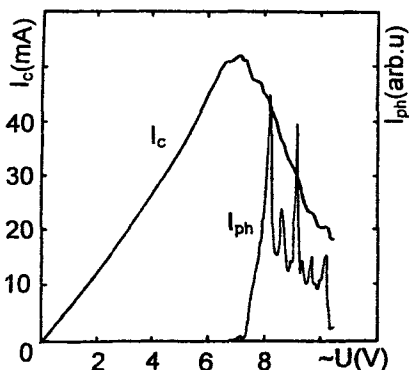


Figure 4. Dependences of the conduction current (I_c) and of the light intensity (I_{ph}) on alternating voltage ($f = 500$ Hz) for Au island film deposited on a flat SiO_2 substrate and covered with a stearone overlayer. $T = 300$ K, $\lambda = 582$ nm.

present a subject of active research [12]. In particular, in compounds with non-conjugated bonds, the electroluminescence is attributed to recombination of charge carriers injected into lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO). In IMFs, one should also additionally consider the possibility of light emission mechanisms specific to nanoislands where hot electrons can be generated [4,7].

4 Conclusions

In this paper we have discussed some properties of nanocomposites consisting of metal islands and organic bridges between them. Such composites have an important advantage of comparatively simple preparation. In addition to vacuum evaporation of IMFs considered above, one can also use such inexpensive techniques as spin casting of dilute colloid suspension of nanoparticles [13] and ink-jet printing [14]. In these technologies and in the subsequent deposition of organic overlayers one can take advantage of self-organization of both metal islands and organics components. The planar metal island-organic nanocomposites provide a

possibility to obtain point-like (submicron) emission sources which can simultaneously generate electrons and light.

Evidently, the mechanisms of processes that occur in such complex systems require further investigations. The questions to be clarified in more detail include the structure of the emission centers, the size effects in metal nanoparticles, the processes in organic molecules and their complexes as well as at their interfaces with the islands. There exist broad opportunities for improving electron and light emission characteristics of such composites (intensity, spectrum, stability etc.) and their switching properties.

5 Acknowledgements

This work was supported by the Ministry of Ukraine for Education and Science (Project # 206 of 14.06.2000). We are indebted to Mrs. O. L. Fedorovich and Dr. V. N. Byckov for their help in the preparation of the typescript.

References

1. Borziak P. G., Sarbej O. G., Fedorovitsch R. D., Neue Erscheinungen in sehr duennen Metallschichten, *Phys. Stat. Sol.* **8** (1965) pp. 55-58.
2. Fedorovich R. D., Naumovets A. G., Tomchuk P. M., Hot electrons in nanoparticles: a model of electron and light emission from island metal films. In *Physics, Chemistry and Application of Nanostructures*, ed. by Borisenko V. E., Filonov A. B., Gaponenko S. V., Gurin V. S. (World Scientific, Singapore, 1999) pp. 145-147.
3. Fedorovich R. D., Naumovets A. G., Tomchuk P. M., Electronic phenomena in nanodispersed thin films, *J. Phys.: Condens. Matter* **11** (1999) pp. 9955-9967.
4. Fedorovich R. D., Naumovets A. G., Tomchuk P. M., Electron and light emission from island metal films and generation of hot electrons in nanoparticles, *Phys. Rep.* **328** (2000) pp. 73-179.
5. Zinke-Allmang M., Phase separation on solid surfaces: nucleation, coarsening and coalescence kinetics, *Thin Solid Films* **346** (1999) pp. 1-68.
6. Fedorovich R. D., Naumovets A. G., Ostranitsa A. P., Tomchuk P. M., Electron emission from regular chain-like island structures, *Int. J. Electronics* **69** (1990) pp. 179-183.
7. Borziak P. G., Dan'ko D. B., Fedorovich R. D., Kiyayev O. E., Naumovets A. G., Current-stimulated electron and photon emission from adlayer-covered nanomaterials, *Prog. Surf. Sci.* **53** (1996) pp. 171-178.
8. Pagnia H., Sotnik N., Bistable switching in electroformed metal-insulator-metal devices, *Phys. Stat. Sol. (a)* **108** (1988) pp. 11-65.

9. Komar A. P., Komar A. A., Molecules and complexes of molecules and atoms as waveguides of electron waves, *Zhurn. Tekhn. Fiz.* **31** (1961) pp. 231-237 (in Russian).
10. Chen J., Reed M. A., Rawlett A. M., Tour J. M., Large on-off ratios and negative differential resistance in a molecular electronic device, *Science* **286** (1999) pp. 1550-1552.
11. Owen A. E., Le Comber P. G., Hajto J., Rose M. J., Snell A. J., Switching in amorphous devices, *Int. J. Electronics* **73** (1992) pp. 897-906.
12. Kalinowski J., Electroluminescence in organics, *J. Phys. D: Appl. Phys.* **32** (1999) pp. R179-R250.
13. Andres R. P., Bielefeld J. D., Henderson J. I., Janes D. B., Kolagunta V.R., Kubiak C. P., Mahoney W. J., Osifchin R. G., Self-assembly of a two-dimensional superlattice of molecularly linked metal clusters, *Science* **273** (1996) pp. 1690-1693.
14. Yamaguchi E., Sakai K., Nomura I., Ono T., Yamanobe M., Abe N., Hara T., Hatanaka K., Osada Y., Yamamoto H., Nakagiri F. T., A 10-in surface-conduction electron-emitter display, *J. Soc. Inform. Display* **5** (1997) pp. 345-348.

SIZE-CONTROL OF SMALL METAL CLUSTERS AND NANOPARTICLES IN ZEOLITES: SILVER AND COPPER IN MORDENITES WITH VARIABLE $\text{SiO}_2/\text{Al}_2\text{O}_3$ MOLAR RATIO

V. S. GURIN

*Physico-Chemical Research Institute, Belarusian State University
Leningradskaja str. 14, 220080 Minsk, Belarus*

E-mail: gvs@shp.bsu.unibel.by

N. E. BOGDANCHIKOVA, V. P. PETRANOVSKII

CCMC-UNAM, Apdo. Postal 2681, 22800, Ensenada, B.C. Mexico

E-mail: nina@ccmc.unam.mx; vitalii@ccmc.unam.mx

Zeolites with less-than-nanometer cavities within the regular crystal lattice incorporate silver and copper species produced by the hydrogen reduction of the ion-exchanged matrices. The metals were stabilized within the mordenite in the form of both few-atomic clusters and nanoparticles (< 50 nm). The clusters and nanoparticles were discovered by means of diffuse reflectance spectroscopy (DRS). Their contribution into optical absorption was calculated by the Mie theory for nanoparticles and with the quantum chemical *ab initio* MOLCAO method for small clusters.

1 Introduction

One of the overriding problem in the field of metal nanoparticles through the years of their intensive research is regulation of size since a genuine feature of the nanoparticles is size- and shape-dispersion. The physical nature of this feature consists of difference of particle properties under changes of number of atoms, diversity of isomers of same nuclearity, and flexibility of metallic bonds. All that provides impossibility to produce mono-sized metal nanoparticles. However, in the range of lower sizes, when metal aggregates belong to the clusters with certain nuclearity and geometry, the situation can be resolved as a result of more pronounced size-dependence of cluster stability. Such beautiful species as mononuclear Au_{55} cluster can be prepared as a result of its high symmetry and stability with the ligand capping [1].

An external constraint can be attained when a cluster is introduced into a small cavity, which is to prevent its further growth and make troubled interaction with an environment. An example of this process is intra-zeolite-produced metal clusters. Size of the latter, evidently is restricted by the cavity dimensions those are very variable in zeolites, and could be the means of size-control. An introduction of a metal in the zeolite matrices is easy to do due to their efficient ion-exchangeability.

Metal ions can be transformed into metal atoms under reduction, and further nucleation and growth result in some few-atomic clusters with a cavity-constrained nuclearity. A successful synthesis of such species, e.g., identified as Ag_8 , has been performed recently [2] by tuning zeolite properties and reduction conditions.

In this paper we summarize experimental data indicating the role of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (MR) of mordenite upon the state of reduced silver and copper clusters and nanoparticles. This parameter (MR) of zeolites retains completely the regular lattice structure, but provides a wide range of acidity variation of the matrix and ion-exchange capacity. The experimental findings are analyzed taking into account calculations of the cluster properties by a quantum chemical *ab initio* method and estimations of the optical absorption with the simple Mie theory.

2 Experimental methods and theoretical models

Protonated forms of mordenites with MR varied from 10 to 206 were supplied by TOSOH Corporation, Japan. Ag- and Cu-containing samples were prepared by the ion exchange in the corresponding aqueous solutions of metal nitrates. The suspensions were filtered, washed and dried. Silver and copper concentration in the final samples was kept in the range of 0.5-2 wt.%. Heating in hydrogen at 293-773 K resulted in the reduction of metal ions. The prime reduced form in the case of silver is atomic $\text{Ag}(0)$, but in the case of copper a number of intermediate-valence species exist in line with $\text{Cu}(0)$. The materials with reduced metals were studied by diffuse reflectance spectroscopy (DRS) recorded with a Varian Cary-300 spectrometer with subsequent Kubelka-Munk processing.

We have calculated selected geometric structures with different symmetry those can be considered as initial points in search of most probable clusters fitting the mordenite channels (with the cross section 0.63×0.70 nm). The examples presented here are the most symmetrical $\text{M}_8 - \text{O}_6$ cube, and a special 3D polyhedron with C_{2v} point group symmetry. Fig. 1 depicts the structures

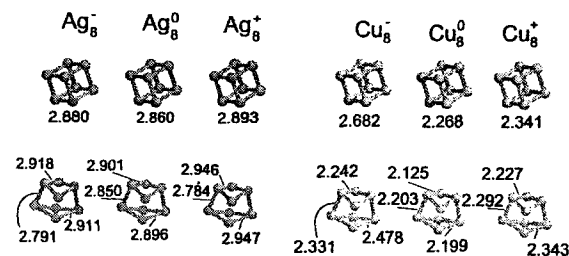


Figure 1. Geometry of the Ag_8 and Cu_8 cluster models and the interatomic distances in the optimized structures.

calculations were carried out by restricted and unrestricted (for open shells) self-consistent field Hartree-Fock methods within the molecular orbital – linear combination of atomic orbitals (MOLCAO) approach. Ground states were calculated, and electronic transitions were estimated from energies of frontier orbitals. A basis sets were used with the effective core potentials [3] with 19

valence electrons and 28-electron core for Ag atoms, while all-electronic basis of STO-3G and 6-31G** types were found to be more appropriate for Cu atoms. The calculations were performed with the HONDO7 and GAMESS(US) programs.

3 Experimental results

The DRS data for the Ag-mordenite samples reduced at the temperature providing maximum intensity of the peaks in UV region are shown in Fig. 2. The appearance of these maxima depends on MR value; and the silver reduction for some of MR takes place beginning from 300 K. The principal peaks are at 280-285 and 318-323 nm. In the range of wavelengths 370-450 nm the broad absorption band is developed. The medium values of MR provide the pronounced UV maxima, while for low and high MR these maxima appear to be much weaker. They were assigned to the silver clusters with nuclearity Ag_8 according to their observation in solutions [4] and the mass-spectroscopic detection [5]. The clusters of other nuclearities, Ag_n with $n < 8$ and $n > 8$, have essentially shifted peak positions. The long-wave broad absorption band can be associated with silver nanoparticles (with sizes in the range of 1-5 nm) [6]. They are rather trivial product in different Ag-containing systems with the optical appearance as the plasmon resonance, usually described by the Mie theory.

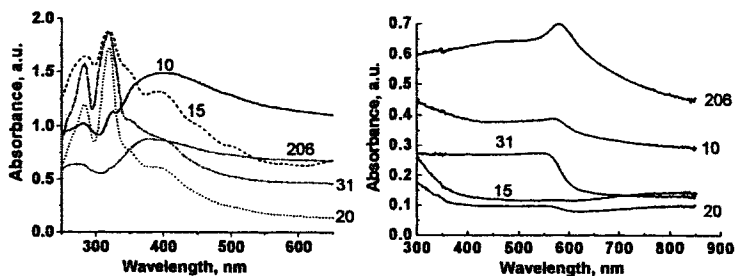


Figure 2. Spectra of DRS for a series of Ag (left) and Cu (right) - exchanged and reduced in hydrogen at 200°C (Ag) and 450°C (Cu) mordenites with various SiO_2/Al_2O_3 molar ratio (given by the numbers at curves).

The above sharp UV peaks are inherent to the molecular-like clusters. We attribute the process of their formation and stabilization to the features of mordenite. The mordenite matrix provides appropriate “medium” for the silver reduction, and cavities keeps the reduction product. In some other zeolites with similar sizes of cavities (erionite, beta, LTL) the clusters with slightly variable position of absorption bands can be formed also. A size of Ag_8 corresponds approximately to the cavity dimension. Silver reduced in inappropriate medium aggregates out of cavities and forms big particles. The acidity of the matrix (governed by MR) is the tool optimizing stability and concentration of the clusters.

The DRS of Cu-mordenites reduced at the optimum temperature are shown in Fig. 2. The principal absorption band peaked at 580-600 nm appears under the lowest MR = 10, disappears under MR = 15, begins to be seen under R = 20, and again successfully develops under MR = 31, remaining up to the highest MR = 206. Moreover, when it is absent (MR = 15) or very weak (MR = 20), we see the broad absorption band with $\lambda > 600$ nm and the common rising of the spectra occurs in short-wavelength range, $\lambda < 400$ nm.

An assignment of these spectral features was carried out taking the familiar data for some solid state systems containing ultrafine copper. The broad long-wave band (which presents also in all samples before reduction) is nothing but Cu^{2+} ions [7], location of which in a set of intrazeolite positions results in broadness of this band. The plasmon resonance in copper nanoparticles enters usually the range 550-600 nm. We confirmed its position and shape by calculations of the Mie-absorption for separate spherical copper particles located in a model medium with the dielectric constant ϵ_0 . The optical constants of Cu were used from [8]. Their size-dependence was accounted just through the imaginary part by the limitation of the mean free path length of electrons [9].

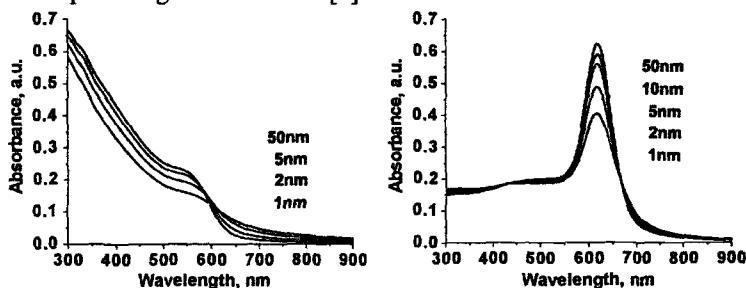


Figure 3. Calculated absorption spectra of Cu nanoparticles in the medium with $\epsilon_0=1$ (left) and $\epsilon_0=5$ (right) for particles with sizes shown correspondingly to the position of curves.

Fig. 3 depicts the calculated absorption spectra for a series of sizes and different ϵ_0 ($\epsilon_0 = 1$ and $\epsilon_0 = 5$; close to the typical values for air and for silicate materials). These data display the remarkable effect of the main parameters used (size and medium dielectric constant) not only upon position of the maximum but also upon the shape of the absorption feature. It evolves from the shoulder in the case of low ϵ_0 values and small size to the pronounced peak for high ϵ_0 and large particles. Thus, we can associate the observed spectra with variation of size of copper particles and their position in mordenite. However, the particles of this size range (even 1 nm) could not fit the cavities. They are located, possibly, either on microcrystal surface (this version can correspond to low ϵ_0) or inside mordenite in the mesopores (but not in the crystalline cavities unlike the above Ag_8). The copper nanoparticles produced in mordenites with the lowest and the highest MR (possessing the lowest acidity) have the bigger size and are surrounded by the mordenite medium.

Thus, our experimental findings with the reduction of Ag- and Cu-exchanged mordenites show the possibility of size variation of the particles produced from the few-atomic clusters to the nanoparticles with bulk-like properties. Below we simulate the clusters assigned with *ab initio* quantum chemical calculations.

4 Quantum chemical calculations

Data obtained for the couple of cluster structures presented (Fig. 1) show that the neutral cubic Ag_8 clusters are more stable than the C_{2v} isomers (the difference is ~ 0.3 eV), but positively and negatively charged clusters have almost the same value of the total electronic energy. Moreover, the electronic density distribution in the charged O_h structures distorts down to $\text{C}_1 \sim \text{C}_{2v}$ symmetry. This means that a coexistence of different isomers is possible at ambient temperature. Electronic transitions estimated for this family reveal that the neutral ones have very high energies of the first allowed transitions, while the transitions for the charged clusters are more reasonable and can match experimental observations: Ag_8^+ of C_{2v} symmetry has the first transitions corresponding to $\lambda = 323$ and 299 nm. They have the best agreement with the above observed peaks. Thus, we consider this cluster as a candidate for species stabilized in the mordenite cavities. This cluster possesses also rather short Ag-Ag interatomic distance, and, consequently, it can easier enter a cavity without large distortion. Our recent EXAFS refinement [2] evidences the similar structure for silver clusters in erionite having the cavities with circular cross section of near dimensions.

The calculations for Cu_8 clusters showed more complicated relations of “cluster charge-symmetry distortion”: a common feature is the significantly higher distortion than in the case of Ag_8 counterparts. The difference in stability of the structures is also more evident. Interatomic Cu-Cu distances in the clusters with initial C_{2v} geometry are minimum, and for O_h cluster the strong effect of charge upon interatomic Cu-Cu distances was observed (Fig. 1). However, sizes of these Cu_8 clusters is less than corresponding Ag_8 isomers, that hardly can argue on the successful fitting of them in the mordenite cavities. We would like to emphasize also that almost all types of Cu_8 have numerous transitions with $\lambda < 250$ nm that is difficult for their unambiguous decoding because the zeolite matrix absorption interferes with them. In the other range we did not observed any experimental DRS features those could be assigned to small copper clusters (Section 3). Nevertheless, these data do not exclude possibility of production of some other Cu_n in mordenite with an appropriate tuning of the preparation conditions.

5 Conclusions

The Ag- and Cu-ion exchanged mordenite matrix can be used for production of clusters and nanoparticles, size of which is controlled by the mordenite MR value.

In the case of Ag-mordenite system both mono-sized clusters Ag_8 and nanometer-range particles were produced, while in the Cu-mordenites only the latter appeared in the range of experimental conditions studied. Optical absorption of the Cu particles was simulated by their plasmon resonance dependent explicitly on the medium dielectric properties. The models of Ag_8 and Cu_8 clusters were calculated by *ab initio* MOLCAO method. The positively charged 3D polyhedron with C_{2v} symmetry was found to satisfy the observed DRS optical data.

6 Acknowledgements

The authors acknowledge funding for this research by CONACYT, Mexico, through grants № 32118-E, 31366-U and 1 E120.2403.

References

1. Schmid G., *Chem. Rev.* **92** (1992) 1709.
2. Ogden J. S., Bogdanchikova N. E., Corker J. M., Petranovskii V. P., *Eur. J. Phys. D* **9** (1999) 608.
3. Hay P. J., Wadt W. R., *J. Chem. Phys.* **82** (1985) 299.
4. Henglein A., *Ber. Bunsenges. Phys. Chem.* **99** (1995) 903; **101** (1997) 1562.
5. Fedrigo S., Harbich W., Buttet J., *Phys. Rev. B* **47** (1993) 10706.
6. Kreibig U., Vollmer M., *Optical properties of metal clusters* (Springer, 1995).
7. Lamberti C., Borgida S. et al., *J. Phys. Chem. B* **101** (1997) 344.
8. Johnson P. B., Christy R. W., *Phys. Rev. B* **6** (1972) 4370.
9. Bohren C. F., Huffman D. R., *Absorption and scattering of light by small particles* (J. Wiley & Sons, New York, 1983).

FORMATION OF ULTRADISPERSE BIMETALLIC PARTICLES BY REDOX PROCESSES IN AQUEOUS SOLUTIONS

YU. A. FEDUTIK, YU. V. BOKSHITS, G. P. SHEVCHENKO

*Physico-Chemical Research Institute, Belarusian State University
220050 Minsk, Belarus*

E-mail: Shevchenko@fhp.bsu.unibel.by

Two preparation method of ultradisperse Ag/Cu bimetallic nanoparticles are presented. They include the reduction of insoluble metal compounds or metal ions in aqueous solutions. the reduction process is monitored by optical absorption spectroscopy.

1 Introduction

Nanosize metal particles are intermediate species between the bulk metals and individual atoms, thus being of considerable theoretical and practical interest due to their unique properties differing from the bulk metals. Until recently, the systems with noble metal nanoparticles were intensively studied, and only in the last years paper concerning bimetallic system, appeared [1-5]. Bimetallic systems are more promising, as their properties depend both on chemical composition and particle structure. The four types of structures are expectable for bimetallic particles: (i) a homogeneous or nearly homogeneous solid solution of the metals; (ii) an intermetallic compound; (iii) nanoheterogeneous 'core-shell' structures and (iv) aggregated nanodomains (clusters) of individual metals.

This paper presents the research toward investigating and experimentally justifying the bimetallic Ag-Cu nanostructure formation by the electroless reduction of insoluble metal compounds and metal ions in aqueous solutions.

2 Methods

In order to control the particle structure several methods were used to produce colloidal solutions of bimetallic particles: 1) mixing of individual Ag and Cu sols, 2) co-reducing of Ag^+ and Cu^{2+} ions in solution, 3) reduction of ultradisperse particles of AgI-CuI solid solution. An excess of sodium borohydride was employed as the reducing agent.

To produce bimetallic particles by the reduction of insoluble Ag and Cu compounds the procedures were developed which yield stable colloidal AgI and CuI and AgI-CuI solid solutions containing 5×10^{-4} mol/l of the disperse phase. The particle size was about 10-15 nm. X-ray diffraction measurements evidenced that

AgI-CuI colloidal particles were formed as the substitution solid solution based on the cubic (γ) AgI modification.

Optical spectroscopy, X-ray diffraction and electron microscopy techniques were used to investigate the resulting sols of metallic and bimetallic particles.

3 Results and discussion

The bimetallic sols produced by mixing of individual silver and copper sols revealed the presence of the two particle fractions characterized by the particle size distribution similar with the distribution for the individual silver and copper particles ($d_{\text{mean Ag}} = 5 \text{ nm}$, $d_{\text{mean Cu}} = 15 \text{ nm}$). The results of spectroscopic investigation suggest that two particle types occur: the two absorption peaks at 420 and 565 nm can be attributed to silver and copper colloidal particles, respectively (Fig. 1).

Ag-Cu particles produced by co-reduction of respective ions have approximately same sizes ($d_{\text{mean}} = 6 \text{ nm}$, the standard deviation $\sigma = 2.5 \text{ nm}$). A shoulder-like fall-off in the range 450-600 nm instead of the pronounced absorption bands characteristic for the individual copper and silver particles can argue that a new type of nanoparticles being formed (Fig. 1). An oxidation of bimetallic Ag-Cu particle was found to be inhibited as compared to that of copper particles. This inhibition effect can occur due to the protective layers of Ag(I) and Cu(I) hydroxides formed, perhaps, as the result of silver particle oxidation by Cu(II) ions [6].

The changes in the optical absorption spectrum during the reduction of ultradisperse AgI-CuI solid solution particles (Fig. 2) showed that the bands in the visible region, peaking at 420 and 510 nm, gradually come together and transform into the single band peaking at 420 nm. The similar initial formation of two absorption bands coming gradually together was observed during the reduction of individual AgI and CuI colloids. The position of absorption maxima and the values of optical density for the metal sols formed depend on the nature of a particular iodide. In the case of AgI the absorption bands enter a shorter wave region (410 and 500 nm) and gradually transform into the single band with $\lambda_{\text{max}} = 435 \text{ nm}$. The optical density is concurrently growing under this transformation. No single absorption band formation was observed with CuI colloid reduction, but the optical density was somewhat increased. A low rate of CuI reduction can be reason of that observation. The occurrence of two absorption bands in optical spectra followed by their transformation into a single band during reduction of AgI colloidal solution has been described earlier [7], and it can be associated with the formation of "core(AgI)-shell(Ag)" structures. The reduction of AgI-CuI solid solutions seems also to be connected with similar structures. The reduction is complete, this process yields nanoheterogeneous bimetallic particles.

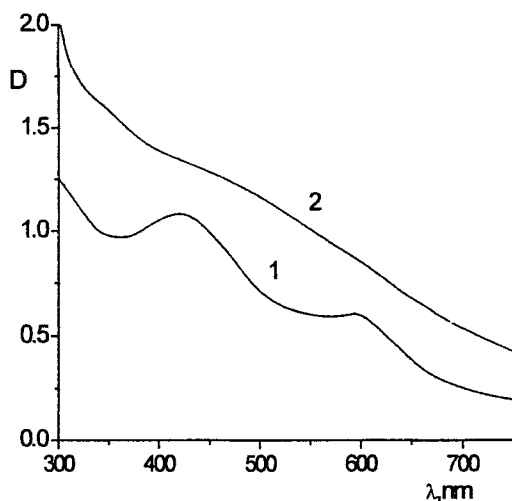


Figure 1. Absorption spectra of Ag-Cu sols ($\text{Ag/Cu}=1/5$), produced by: 1 - mixing of individual Ag and Cu sols; 2 - co-reduction of Ag(I) and Cu(II) ions in solution.

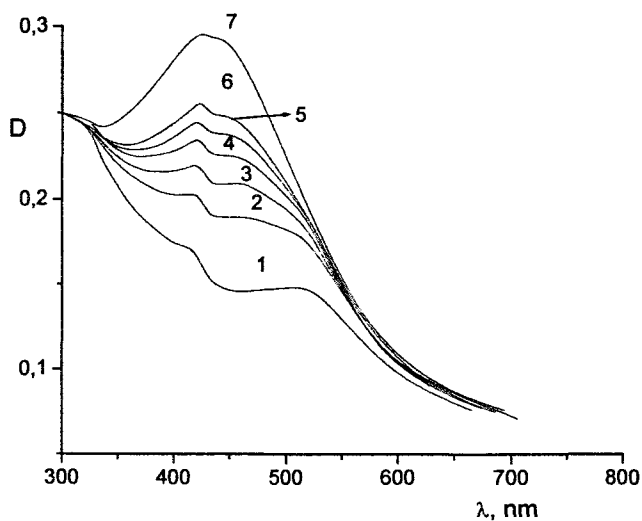


Figure 2. Changes in the optical absorption spectra of AgI-CuI ($\text{Ag/Cu}=1/1$) colloidal solution with time in the course of the reduction: 1 – 5 min, 2 – 10 min, 3 – 15 min, 4 – 20 min, 5 – 25 min, 6 – 30 min, 7 – 60 min.

Thus, we demonstrated the possibility to produce ultradisperse bimetallic particles by electroless reduction of insoluble metal compounds and metal ions in aqueous solution. AgI-CuI ultradisperse particles were reduced through a solid-phase mechanism via formation of intermediate "core(AgI-CuI)-shell(Ag-Cu)" structures.

References

1. Loginov A. V., Gorbunova V. V., Boitsova T. B., *Zhurn. Obshch. Khim.* **67** (1997) 189.
2. Mulvaney P., Giersig M., Henglein A., *J. Phys. Chem.* **97** (1993) 7061.
3. De G., Mattei G., Mazzoldi P. et al., *Chem. Mater.* **12** (2000) 2157.
4. Link S., Wang Z., El-Sayed M., *J. Phys. Chem. B* **103** (1999) 3529.
5. Catalano M., Carlino E., De G., *Phil. Mag. B* **76** (1997) 621.
6. Avraamides J., Precious Metals: Mining, Extracting and Process. In *Proc. Int. Symp. AIME Ann. Meet.* (Warrendale, Los Angeles, 1984) pp. 301-305.
7. Shevchenko G. P., Afanas'eva Z. M. In: *Physics, Chemistry and Application of Nanostructures* (World Scientific, Singapore, 1999) 233.

POLYELECTROLYTE MICRO- AND NANOCAPSULES AS MICROCAGES FOR CHEMICAL REACTIONS IN RESTRICTED VOLUMES

G. B. SUKHORUKOV, I. L. RADTCHENKO, H. MÖHWALD

*Max-Planck-Institute for Colloids and Interfaces Research
14424 Golm/Potsdam, Germany*

E-mail: gleb@mpikg-golm.mpg.de

A novel approach to incorporate different polymers into micro- and nanocapsules fabricated by means of layer-by-layer (LbL) adsorption of oppositely charged polyelectrolytes on colloidal particles is proposed. This method comprises two stages. At first, the polymers, which are supposed to be incorporated, precipitate on the surface of colloidal particles. This can be done either by complexation of polyelectrolytes with multivalent ions or by adding miscible non-solvents. Then stable LbL assembled polyelectrolyte shells are formed. After the core decomposition the inner polymer molecules are released from the wall but captured by the outer shell and floating in the capsule interior. The possibilities to encapsulate a wide class of charged and non-charged polymers were demonstrated on the examples of sodium poly(styrene sulfonate) (PSS) like a polyanion, poly(allylamine hydrochloride) (PAH) like a polycation and dextrane like non-charged water soluble polymer.

1 Introduction

The development of functional colloidal particles gains interest in different areas such as biosensing, catalysis, biotechnology, medicine, ecology and others. One possible way to functionalise colloidal particles intensively elaborated in the last few years is layer-by-layer adsorption of oppositely charged macromolecules. Multilayer film assembly provides a defined shell composition on the colloidal core. The thickness of the shell as a function of the assembled layer number can be tuned in the nanometer range. Variety of materials, such as synthetic polyelectrolytes, proteins, DNA, inorganic particles and lipids, can be used as building blocks to prepare shells on colloids with desired properties [1,2]. This method of LbL assembly can be applied to coat various charged particles, such as organic and inorganic colloids, biological cells or drug nanocrystals.

The decomposition of the colloidal core can lead to formation of hollow polyelectrolyte capsules [2-5]. Their size and shape is determined by the colloidal template and can range from 0.1 to 10 μm . The amount of material introduced in multilayers can be tuned in mg per m^2 of surface area. One of the significant properties of these capsules is their selective permeability. The molecular weight cut-off for capsule wall permeation usually can be varied from 500 to 50,000 whereas small molecules and ions can readily diffuse through the capsule wall [4].

Using multivalent ions for multilayer build-up leads to dissolvable multilayer formation. In relation to polyelectrolyte capsules the possibility to vary the stability of the capsule wall composed of multilayers opens perspectives to control capsule degradation.

Aim of this work is to develop an advanced method to introduce different types of macromolecules into polyelectrolyte capsules. In order to achieve it we fabricate double wall capsules with subsequent load by decomposition their inner wall at conditions where the outer wall is stable.

2 Results and discussions

Controlled precipitations of polymers on colloidal particles were obtained by two different approaches illustrated in Fig. 1. At first, the suspension of melamine-formaldehyde (MF) particles ($5\ \mu\text{m}$) was mixed with Me^{3+} -ions (a), then the

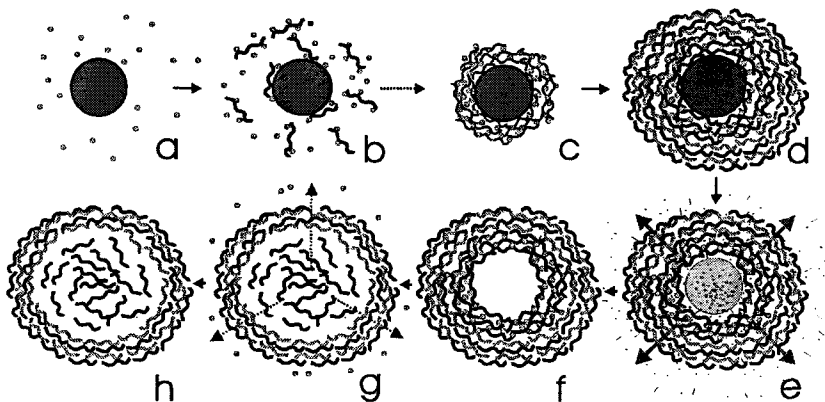


Figure 1. Schematics of controlled precipitation of polymers on colloidal particles.

polyanion PSS was added, which leads to the formation of precipitates $\text{Me}^{3+}/\text{PSS}$ (b). 1 ml suspension of MF-particles (concentration $5 \times 10^8\ \text{cm}^{-3}$) with $5 \times 10^{-3}\ \text{M}$ $\text{Y}(\text{NO}_3)_3$ was continuously stirred during dropping ($10\ \mu\text{l}$) of PSS labelled with rhodamine (Rd) solution (1mg/ml) until the final PSS-Rd concentration reached a certain value, that, as estimated, is sufficient to form approximately 80 monolayers on top of MF-particles. The PSS-Rd/ Y^{3+} complex is slowly formed. After 10-15 minutes the particles were centrifuged (c), and the amount of PSS-Rd molecules not bound to the particles, was measured by supernatant fluorescence. Remarkably, the amount of PSS-Rd absorbed to MF-particles is about 80-85 %. It should be noted that we always have an excess of charges for Y^{3+} in order to complex all PSS-Rd molecules with metal-ions. The MF-particles were observed by confocal microscopy. The fluorescence coverage of MF-particles is rather smooth. There are almost no fluorescent species outside the particles. Fluorescent PSS-Rd is

homogeneously distributed on the surface of MF-particles. Positively charged polyelectrolytes also could be used accordingly to this scheme. To the suspension of MF-particles and citric acid the polycation PAH-Rd that forms insoluble complex with citric acid was added by drop-wise. The final concentration of PAH-Rd was equal to the PSS-Rd one in the first case. The confocal microscopy observations show the homogeneous coverage of MF-particles by the PAH-Rd/citrate complex.

A selective permeability and dissolution of precipitated macromolecules give an opportunity for encapsulation of macromolecules into polyelectrolyte capsules. Indeed, assembly on colloid particles might comprise two stages. The first stage is controlled precipitation of a unstable shell composed of multivalent ions and polyelectrolytes or just polymers, and the second stage consists of assembling the above stable polyelectrolyte multilayers, for instance, PAH/PSS (d). After colloidal core decomposition (e) the capsules have the two-shell structure (f). The precipitated polymer might be solved into the capsule interior at a condition where the outer shell is stable (g). Multivalent ions are small enough to penetrate through polyelectrolyte multilayers comprising the outer shell whilst polymers used for inner shell build-up can not be expelled due to their high molecular weight. Thus, these polymers are captured inside the capsule as freely floating molecules (h), (f).

The idea described has been used to load the polyelectrolyte capsules with charged and noncharged macromolecules. Dissolution of MF-particles in 0.1M HCl leads to hollow capsule formation. Capsules with Y^{3+} /PSS-Rd complexes were treated in 2M NaCl and 0.1M EDTA. The capsules containing citrate/PAH-Rd were exposed to basic pH conditions. As mentioned above, by these conditions precipitated polymers are dissolved. The ions are released and removed from the capsule suspension. The confocal images of the capsules after inner shell decomposition for cases Y^{3+} /PSS-Rd are shown in Fig. 2. At this stage, the capsule interior is filled with free fluorescently labelled polymers.

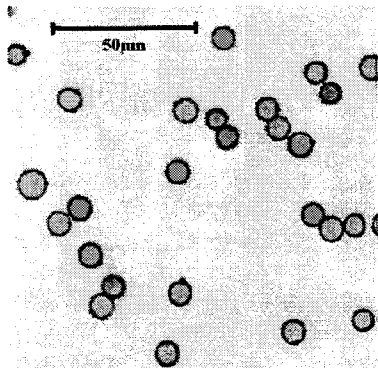


Figure 2. Confocal microscopy image of the capsules filled with labeled PSS.

Capsules containing encapsulated PSS are significantly swollen. Their diameter is about 8-10 μm while the initial size of template MF-particles was only 5.6 μm . It should be mentioned that just after core decomposition the capsules size is close to the initial one. Therefore, the capsules swell when the PSS molecules are released from the wall to the interior due to the osmotic pressure difference [12]. The concentration of free polymer molecules for all three cases inside the capsules was estimated by the integrated fluorescence intensity from the interior revealed by confocal microscopy. It gives us values of approximately 0.1 monoM polymer concentration in rather good agreement with the estimations based on assumption that all polymer

molecules are finally dissolved to the interior. This means that we have about 10^{-12} g of polymer per capsule. Actually, the amount of loaded polymer is determined by the ratio between polymer and colloidal particle concentrations during the controlled precipitation.

This approach is based on composite shell fabrication with subsequent decomposition their inner shell at conditions where the outer shell is stable. A lot of different materials such as various polyelectrolytes, proteins, DNA, polysaccharides and inorganic particles can be first precipitated on the surface of colloidal particles and then loaded into the capsules. Size and shape of these capsules are defined by initial templates. Micro- and nanostructures with predictable properties such us controlled concentration of a given material inside can be created. Encapsulation of polyelectrolytes can establish a pH-gradient across capsule walls due to a Donnan potential. The pH value in the capsule should be close to the pK value of the encapsulated polymer [4]. Such modified capsules are also supposed to be used as microcontainers and microreactors to perform the chemical reactions in their restricted volume.

3 Acknowledgements

The authors thank Dr. E. Donath (Max-Planck-Institute of Colloids and Surfaces, Potsdam) for stimulating discussions. This work was partially supported by the BMBF grant 03C0293A1.

References.

1. Sukhorukov G. B., Donath E., Lichtenfeld H., Knippel E., Knippel M., Budde A., Möhwald H., *Colloids and Surf. A* **137** (1998) 253.
2. Sukhorukov G. B., Donath E., Davis S. A., Lichtenfeld H., Caruso F., Popov V. L., Möhwald H., *Polym. Adv. Technol.* **9** (1998) 759.
3. Donath E., Sukhorukov G. B., Caruso F., Davis S., Möhwald H., *Angew. Chem. Inter. Ed. Engl.* **37** (1998) 2201.
4. Sukhorukov G. B., Brumen M., Donath E., Möhwald H., *J. Phys. Chem.* **103** (1999) 6434.
5. Voigt A., Lichtenfeld H., Sukhorukov G. B., Zastrow H., Donath E., Bäuml H., Möhwald H., *Ind. & Eng. Chem. Res.* **38** (1999) 4037.

EMPLOYMENT OF THE LAYER-BY-LAYER TECHNIQUE FOR THE FORMATION OF POLYMER-CORE TiO₂-SHELL PARTICLES AND TiO₂ HOLLOW SPHERES

A. S. SUSHA

*Physico-Chemical Research Institute, Belarusian State University
220050 Minsk, Belarus*

E-mail: a_susha@yahoo.com

N. A. SHKORIK

*Institute of General and Inorganic Chemistry of The National Academy of Science of Belarus
220074 Minsk, Belarus*

E-mail: n_shkorik@aport2000.ru

R. A. CARUSO, F. CARUSO

*Max Planck Institute of Colloids and Interfaces
D-14424 Potsdam, Germany*

E-mail: frank.caruso@mpikg-golm.mpg.de

The possibility of using the layer-by-layer (LbL) technique for the formation of latex-core TiO₂-shell particles and TiO₂ hollow spheres was established. The TiO₂ colloid was produced by the sol-gel technique. Composite organic-inorganic particles were formed by the controlled assembly of the preformed titania nanoparticles in alternation with oppositely charged polyelectrolytes onto latex microspheres. These hybrid core-shell particles were calcined to produce TiO₂ hollow spheres with predetermined diameters.

1 Introduction

Titanium dioxide has very interesting optical, electrical and chemical properties (for example, high refractive index and dielectric constant). TiO₂ has been coated on various inorganic and organic particles for the purposes of catalysis, photocatalysis, photonic crystals preparation, etc. For this reason different coating methods have been used, including the use of titania precursors with subsequent hydrolysis and polycondensation reactions on the template particle surface.

The layer-by-layer (LbL) self-assembly technique is based on the electrostatic association between alternately deposited, oppositely charged macromolecules or nanoobjects [1]. Different organic-inorganic composite particles comprising latex cores and silica nanoparticle [2] or iron oxide nanoparticle multilayer coatings [3] have been fabricated using this technique. An interesting extension of such core-

shell particles has been the subsequent removal of the templated cores resulting in fabrication of hollow capsules [4].

Herein, we present the results on the coating of polystyrene spheres with preformed TiO_2 colloid particles using the LbL deposition technique. The advantages of this technique the nanometer control of both the final diameter of the material, by choice of the initial template diameter, and the multilayer wall thickness, depending on the number of layers deposited. The colloidal core can be subsequently removed, leaving behind a hollow TiO_2 sphere.

2 Methods

2.1 TiO_2 sol preparation

A positively charged TiO_2 colloid (zeta potential +42 mV) was produced by the sol-gel method. TiCl_4 was hydrolysed by ammonia followed by washing, stabilisation by nitric acid, and ultrasonic redispersion. Particles were about 6 nm in diameter and had the anatase crystal structure.

2.2 Core-Shell Particle Fabrication

Before adsorption of the inorganic particles, the surface of the polystyrene (PS) particles was modified by the adsorption of polyelectrolytes [5]. Prior to deposition of positively charged nanoparticles, the polymer spheres were modified by adsorption of PDADMAC/PSS/PDADMAC/PSS* (PE_4), resulting in a negative surface charge for the coated particles [5]. In the next step, the TiO_2 sol was added to the pre-coated latex. After adsorption of inorganic particles or polymer, four centrifugation / wash / redispersion cycles were performed for each layer to remove any excess unabsorbed material.

2.3 Hollow Sphere Fabrication

After the formation of the core-shell particles, the core template was removed to produce hollow spheres of the inorganic material. The samples were dried on glass slides and then heated under N_2 . The gas was then changed to O_2 and the sample heated for 8 h at 500 °C.

* PDADMAC - poly (diallyldimethylammonium chloride), PSS – poly (sodium 4-styrenes sulfonate)

3 Results and discussion

Sol-gel produced TiO_2 nanoparticles were used to coat PS spheres. Uniform coatings were obtained (Fig. 1). A diameter increase of 10 nm per TiO_2/PE_3 multilayer was observed. An increase in the overall diameter of the particles was observed as the number of multilayers deposited increased, highlighting the high level of control over the thickness of the TiO_2 coatings. There was also a roughening of the particle surface as a result of growth of the TiO_2 multilayers.

The ability to coat the smaller template PS particles with TiO_2 nanoparticles by using the LbL technique was also investigated. Figs. 2(a, b) show 210 and 350 nm diameter PS templates coated with three TiO_2 nanoparticle layers, respectively. These smaller PS templates were also uniformly covered, however some aggregation of the resulting core-shell entities was observed.

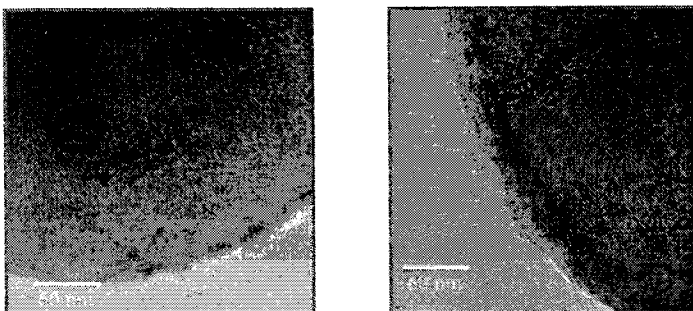


Figure 1. TEM images of 640 nm PS sphere surfaces with 1 (a) and 5 (b) TiO_2 nanoparticle/ PE_3 multilayers.

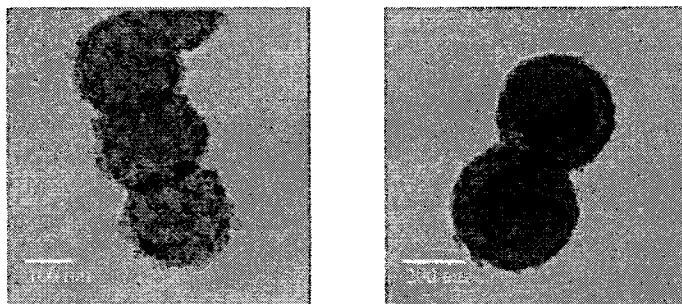


Figure 2. TEM images of core-shell particles consisting of 210 (a) and 350 nm (b) diameter PS core coated with three $[\text{TiO}_2 \text{ nanoparticle}/\text{PE}_3]$ multilayers.

Hollow TiO_2 spheres resulting from calcination of 640 nm PS particles coated with three TiO_2 nanoparticle/ PE_3 multilayers are shown in Fig. 3(a). A shrinkage of 15 % in diameter was observed after calcination. In Fig. 3(b) the smaller hollow TiO_2 spheres can be seen; these were obtained after heating 350 nm PS spheres coated with three positively charged TiO_2 nanoparticle/ PE_3 multilayers. The

average diameter of these spheres is 195 nm, which again represents about a 15 % shrinkage as a result of the template removal process.

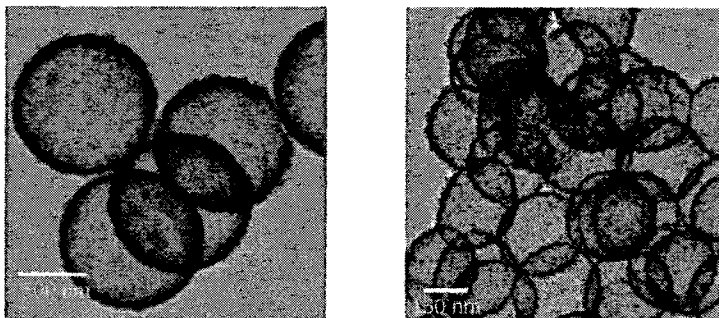


Figure 3. TEM images of hollow TiO_2 spheres formed after calcination of 640 nm (a) and 350 nm (b) PS spheres with three $[\text{TiO}_2 \text{ nanoparticle}/\text{PE}_3]$ multilayers.

N_2 sorption experiments on hollow TiO_2 spheres fabricated with the calcination of PS particles coated with 4 layers of 6 nm TiO_2 nanoparticles (alternating with PE_3 multilayers) were conducted. The specific surface area (SA) from BET analysis of these hollow spheres was $87 \text{ m}^2 \text{ g}^{-1}$, compared to $12.5 \text{ m}^2 \text{ g}^{-1}$ for the core-shell particles, i.e., before calcination.

In summary, composite particles comprising a PS core and well-defined TiO_2/PE multilayer shells and TiO_2 hollow spheres of different diameters (ranging from 200–600 nm) with different wall thicknesses have been prepared using the LbL technique. These colloids are expected to find applications in catalysis and photonics.

4 Acknowledgements

Michael Giersig (HMI-Berlin) is thanked for assistance with the TEM measurements. A. Susha thanks INTAS (grant INTAS-Belarus 97-0250) for the partial financial support.

References

1. Decher G., *Science* **277** (1997) 1232.
2. Caruso F., Lichtenfeld H., Möhwald H., Giersig M., *J. Am. Chem. Soc.* **120** (1998) 8523.
3. Caruso F., Susha A. S., Giersig M., Möhwald H., *Adv. Mater.* **11** (1999) 950.
4. Caruso F., Caruso R. A., Möhwald H., *Science* **282** (1998) 1111.
5. Caruso F., Donath E., Möhwald H. *J. Phys. Chem. B* **102** (1998) 2011.

OBSERVATION OF SINGLE MOLECULE DIFFUSION IN MICRO- AND NANODROPLETS OF POLYMERS ON SURFACES

I. SCHUSTER, F. CICHOS, C. VON BORCZYKOWSKI

*TU Chemnitz, Institut für Physik
D-09107 Chemnitz, Germany*

E-mail: borczykowski@physik.tu-chemnitz.de

J. WRACHTRUP

*Uni Stuttgart, 3. Physikalisches Institut
D-70550 Stuttgart, Germany*

E-mail: j.wrachtrup@physik.uni-stuttgart.de

The diffusion of individual rhodamine 6G molecules in ethylene glycol close to a glass interface has been studied. Diffusion coefficients are analyzed by photon burst analysis and real time wide field microscopy. It is shown by photon burst analysis that the diffusion of dye molecules becomes slower near the interface of the droplet and the glass as compared to the bulk value. We attribute this to anomalous diffusion of molecules close to the interface, due to attachment and detachment of molecules caused by molecule surface interaction. This has been studied by wide field microscopy.

1 Introduction

Diffusion of single molecules in liquids has been extensively studied by confocal microscopy using fluorescence correlation spectroscopy [1-3] or fluorescence burst analysis [4-6] and real time wide field microscopy [7-12]. Correlation techniques allow the determination of diffusion constants of dye molecules in a solvent averaging over a certain number of individual molecules crossing the focus of the confocal microscope. In contrast, the wide field imaging of individual diffusing molecules is a method where the fluorescence from a region of interest is imaged to a CCD camera allowing the reconstruction of diffusion trajectories following one individual molecule over many frames. Single dye tracking by the wide field imaging was demonstrated in different environments (lipids [7,8], gels [9], pure solvents [10], complex biomolecules [11,12]). In the present work fluorescence detection is applied to studies of single molecule diffusion in liquid droplets, wetting a surface.

2 Experimental

The basic model makes the following assumptions: Rhodamine 6G was dissolved in spectroscopic grade ethylene glycol (Aldrich) and diluted to the concentration of 10^{-12} mol/l. A small droplet with a diameter of about one millimeter was deposited on a conventional glass cover slip. The cover slips were cleaned first in spectroscopic grade ethanol (Aldrich) followed by spectroscopic grade water (Aldrich) and dried in a stream of hot air (200 °C). For comparison of the bulk diffusion constants, samples with water instead of the ethylene glycol were prepared by the same way.

We use a home built confocal microscope, mounted on an optical table. The samples were illuminated by the 514 nm line of an argon ion laser which was additionally filtered by a interference band pass filter. Fluorescence was collected by a microscope objective (ZEISS, 100 x, 1.3 NA, oil immersion), filtered by a holographic notch filter (Kaiser Optics) and imaged by a lense (250 mm focal length) to a pinhole (100 μ m diameter) in front of a photo multiplier tube (S20, EMI). Reflected light from the sample was collected in a different detection channel. Details of the set up and analysis are described in a forthcoming paper. Diffusion studies by confocal microscopy are restricted to the analysis of the diffusion components perpendicular to the optical axis of the confocal spot [1]. Since the spot dimensions along the optical axis are much larger (by a factor of about 5) than perpendicular to it, the probe space can be modeled as a long cylinder and the diffusion of the dye molecules through the spot can be treated as 2-dimensional [1,5]. Thus, the experimental situation is similar to the "first passage problem", which describes the diffusion of a particle starting from the center of a given circular area.

3 Results and discussion

To check the data analysis, bulk diffusion constants of rhodamine 6G in water and ethylene glycol were recorded. Fluorescence traces have been measured in large droplets of the solvent far from any interface. Fluorescence burst width analysis results in characteristic diffusion times $\tau_D = 1.1 (\pm 0.2)$ ms for ethylene glycol and $\tau_D = 70 (\pm 50)$ μ s for water. According to the Stokes-Einstein relation

$$D = kT/(6\pi\eta a), \quad (1)$$

with η being the solvent viscosity and a is the spherical diameter of the molecules, the value of τ_D for water should be smaller by a factor 19 than τ_D for ethylene glycol, considering viscosities of $\eta = 0.89$ mPas for water and $\eta = 16.79$ mPas for ethylene glycol [13]. Within the error of τ_D this is in good agreement with the experimental results shown above. From the equation (2) diffusion constants of rhodamine 6G can be calculated to be $D = 2.5 (\pm 1.7) \times 10^{-6}$ cm²/s in water and

$D = 1.6 (\pm 0.3) \times 10^{-7} \text{ cm}^2/\text{s}$ in ethylene glycol which are in good agreement with measurements reported in literature [5].

Cross sections of the sample can be imaged with the confocal microscope in the reflected light or in the fluorescence mode. Fig. 1 shows images of a silicon oil droplet heavily doped with rhodamine 6G as recorded simultaneously in the fluorescence and reflection channel of the confocal microscope. The interference fringes visible in Fig. 1 allow a precise determination of the droplet shape with a thickness resolution of 100 nm.

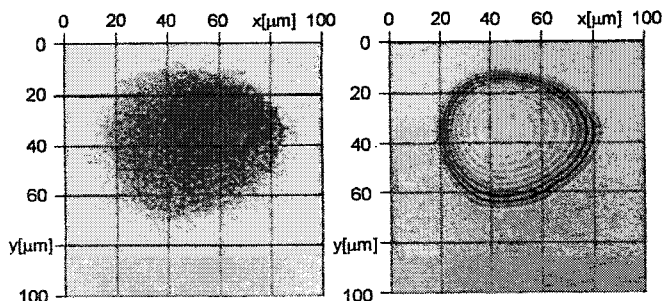


Figure 1. Fluorescence trace for rhodamine 6G in ethylene glycol (0.5 ms per bin).

For liquids with the higher contact angle on glass such as ethylene glycol the distance of the interference fringes is below the optical resolution. Thus the droplet shape was determined with a lower accuracy (1 μm) in this case. Cover slip, droplet and air can be identified in the images by differences in the background luminescence or in reflectivity. By recording time series of such images it was verified that shape and position of droplets of ethylene glycol remain stable over tens of minutes, the time required to record sufficient data for fluorescence burst analysis.

Fluorescence time traces (Fig. 2) were recorded at different positions in the droplet, in the bulk droplet (A) or near the interface (B far from the droplet edge, C at the droplet edge).

The determined characteristic diffusion times and the corresponding diffusion coefficients are summarized in Table 1.

Table 1. Diffusion times τ_D and diffusion coefficients D recorded at different positions in the droplet.

Sample point	τ_D , ms	D , cm^2/s
A	1.1 ± 0.2	$1.6 (\pm 0.3) \times 10^{-7}$
B	1.3 ± 0.2	$1.4 (\pm 0.3) \times 10^{-7}$
C	2.0 ± 0.4	$8.8 (\pm 1.8) \times 10^{-8}$

The measurements point out that the characteristic diffusion times τ_D become longer compared to the bulk values when approaching the liquid-solid interface. Thus the diffusion is slowed down at the edge of the droplet (C) while it is not

significant at (B). The reason for the slow down of the diffusion is the strong interaction of the surface with the liquid molecules which also leads to the well know effect of molecular layering [14]. The observed slow down, however, is not as drastic as expected since the experimental technique we used always samples the emission from a layer more than 100 nm thickness containing molecules not interacting with the surface. This is the case for (B) and also (C) since ethylene glycol has a fairly high contact angle on glass surfaces. The experimental data contain therefore a mean value of the diffusion constant close to the interface and in the bulk. Nevertheless, the effect is stronger in point C, because of the smaller film thickness.

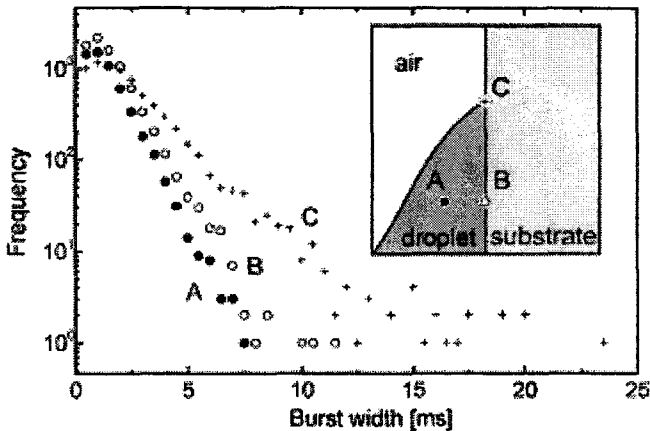


Figure 2. Measured burst width distributions from different regions of the droplet on a glass cover slip. The inset (cross section through the droplet) shows a schematic view of the sample, including points A, B and C where data have been recorded.

We thus conclude that the real interface diffusion coefficients are even smaller than the ones measured here. Correct measurement of the surface diffusion coefficients would require a liquid film thickness of a few nanometers over the range of the confocal spot which was not the case in our experiments. We also note that the technique used is not capable to distinguish between the normal diffusion and the diffusion process which is influenced by attachment periods. First results from the wide field imaging of diffusion trajectories of individual molecules suggest, however, that molecules close to interfaces show anomalous diffusion, i.e. the diffusion is strongly influenced by attachment periods of molecules on the glass surface.

4 Acknowledgements

Financial support of the Deutsche Forschungsgemeinschaft via the Schwerpunkt "Benetzung und Strukturbildung an Grenzflächen" is acknowledged.

References

1. Rigler R., Mets Ü., Widengren J., Kask B., Fluorescence correlation spectroscopy with high count rate and low background: analysis of translational diffusion, *Eur. Biophys. J.* **22** (1993) pp. 169-175.
2. Widengren J., Mets Ü., Rigler R., Fluorescence correlation spectroscopy of triplet states in solution: A theoretical experimental study, *J. Phys. Chem.* **99** (1995) pp. 13368-13379.
3. Eigen M., Rigler R., Sorting single molecules: Application to diagnostics and evolutionary biotechnology, *Proc. Natl. Acad. Sci. USA* **91** (1994) pp. 5740-5747.
4. Chiu D. T., Zare R. N., Biased diffusion, optical trapping, and manipulation of single molecules in solution, *J. Am. Chem. Soc.* **118** (1996) pp. 6512-6513.
5. Ko D.-S., Sauer M., Nord S., Müller R., Wolfrum J., Determination of the diffusion coefficient of dye in solution at single molecule level, *Chem. Phys. Lett.* **269** (1997) pp. 54-58.
6. Osborne M. A., Balasubramanian S., Furey W. S., Klennerman D., Optically diased diffusion of single molecules studied by confocal fluorescence microscopy, *J. Phys. Chem. B* **102** (1998) pp. 3160-3167.
7. Schmidt Th., Schütz G. J., Baumgartner W., Gruber H. J., Schindler H., Characterization of photophysics and mobility of single molecules in a fluid lipid membrane, *J. Phys. Chem.* **99** (1995) pp. 17662-17668.
8. Schütz G. J., Schindler H., Schmidt Th., Single-molecule microscopy on model membranes reveals anomalous diffusion, *Biophys. J.* **73** (1997) pp. 1073-1080.
9. Dickson R. M., Norris D. J., Tzeng Y.-L., Moerner W. E., Three-dimensional imaging of single molecules solvated in pores of poly(acrylamide) gels, *Science* **274** (1996) pp. 966-969.
10. Xu X.-H., Yeung E. S., Direct measurement of single-molecule diffusion and photodecomposition in free solution, *Science* **275** (1997) pp. 1106-1109.
11. Yokota H., Saito K., Yanagida T., Single molecule imaging of fluorescently labeled proteins on metal by surface plasmons in aqueous solution, *Phys. Rev. Lett.* **80** (1998) pp. 4606-4609.
12. Funatsu T., Harada Y., Tokunaga M., Salto K., Yanagida T., Imaging of single fluorescent molecules and individual ATP turnovers by single myosin molecules in aqueous solution, *Nature* **374** (1995) pp. 555-559.
13. *Handbook of Chemistry and Physics, 71st Edition*, ed. by D. R. Lide (CRC Press, Boca Raton, 1990) pp. 6-142-6-147.
14. Yu C.-J., Richter A. G., Datta A., Durbin M. K., Dutta P., Observation of Molecular Layering in Thin Liquid Films Using X-Ray Reflectivity, *Phys. Rev. Lett.* **82** (1999) pp. 2326-2329.

CHEMICALLY GROWN II-VI SEMICONDUCTOR QUANTUM DOTS FOR OPTOELECTRONIC AND PHOTONIC APPLICATIONS

N. P. GAPONIK, D. V. TALAPIN, S. K. POZNYAK, A. S. SUSHA, A. L. ROGACH

*Physico-Chemical Research Institute, Belarussian State University
220050 Minsk, Belarus*

A. EYCHMÜLLER

*Institute of Physical Chemistry, University of Hamburg
20146 Hamburg, Germany*

E-mail: elchem@fhp.bsu.unibel.by

We report on recent progress in the synthesis, surface modification and functionalization, and fabrication of polymer composites, and their use in light-emitting and photonic devices for a number of chemically grown quantum dots: CdSe, CdTe, $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and HgTe.

Quantum dots of CdTe, $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and HgTe were synthesized in aqueous solutions by the reaction of Cd^{2+} (Hg^{2+}) ions and H_2Te in the presence of different thiols (2-mercaptoethanol, 1-thioglycerol, thioglycolic acid, dithioglycerol, mercaptoethylamine) as stabilizing agents [1,2]. $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and HgTe quantum dots showed extremely high (40-50 % at room temperature) photoluminescence (PL) quantum efficiencies (QE) as prepared. The procedure of size-selective precipitation which is widely used for narrowing the particle size distributions has been successfully applied for the separation of fractions of highly luminescent (QE up to 30 %) CdTe nanocrystals.

Quantum dots of CdSe and CdTe were synthesized by the reaction of trioctylphosphine selenide or trioctylphosphine telluride in trioctylphosphine (TOP) solution with dimethylcadmium in the presence of dodecylamine (DDA) in an inert atmosphere. The growth of the nanocrystals occurred in the temperature range of 90-140 °C (CdSe) and 150-210 °C (CdTe) depending on the desired size. This method yielded CdSe quantum dots with diameters ranging from 1.2 to ~2.5 nm and band edge PL with QE ~20 %. Particles of larger sizes were synthesized in three-component mixtures containing hexadecylamine, trioctylphosphine oxide (TOPO) and TOP. In the case of CdTe, the quantum dots show strong band-edge PL with a QE 30-60 %. After isolation from the crude solution the nanocrystal fractions were readily dispersible in a variety of organic solvents such as toluene, n-hexane, chloroform etc.

Fig. 1 shows examples of optical spectra of some quantum dot samples. It also shows the position of their PL maxima depending on their chemical composition and size.

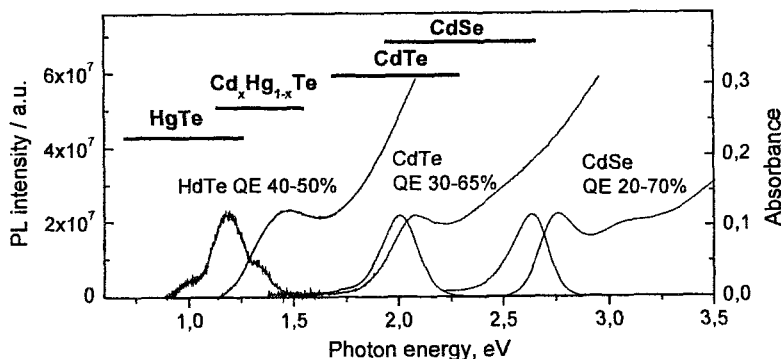


Figure 1. Typical absorption and photoluminescence spectra of a number of II-VI semiconductor quantum dots. The ranges of the positions of the PL maxima achievable by varying the size of the nanocrystals are also shown.

Further modification and functionalization of quantum dots in order to increase their QE and to dissolve them in a larger variety of solvents was realized by surface exchange of the capping groups. Thus, the post-preparative modification of the TOP-capped CdSe nanocrystals by surface exchange with primary amines allowed to increase their PL QE to 50-70 % which was about an order of magnitude larger compared to untreated quantum dots.

The small sizes of the semiconductor quantum dots prevent their use in electronic devices without inserting them into conducting matrices. Due to the specific electrical and optical properties of conjugated polymers they seem to be the most promising conducting matrices for this purpose. The surface of CdSe and CdTe quantum dots can be modified by treatment with aniline or 3-methylthiophene which are the monomers of the well known conducting polymers polyaniline and poly-3-methylthiophene. Further co-polymerization of the modified nanocrystals with aniline or 3-methylthiophene provided a suitable step towards building up composite materials with effective charge transport between the conducting matrix and the quantum dots incorporated.

CdTe/polyaniline and CdTe/polypyrrole composites have also been produced both *via* the treatment of electrochemically prepared polyaniline films with aqueous colloidal solutions of CdTe quantum dots and *via* the electrochemical polymerisation of pyrrole in the presence of CdTe nanocrystals [3]. Electrical characteristics of the above composites as well as of compact layers of CdTe quantum dots sandwiched between an Al-cathode and a SnO_2 -F-anode are shown in Fig. 2. The combination of electron conducting nanoparticles with hole-conducting polymers into a single composite provides an effective charge transport.

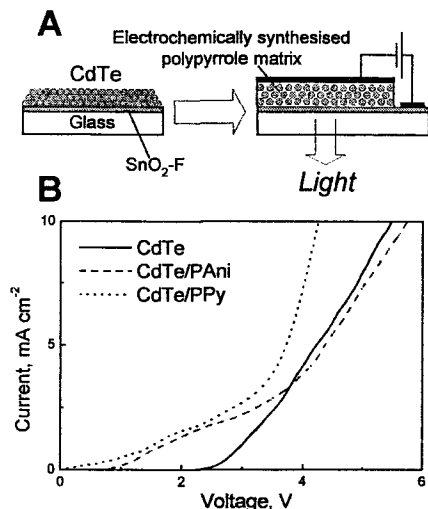


Figure 2. A: Schematic presentation of a light-emitting device based on electrochemically synthesized CdTe/polypyrrole composite.

B: Current-voltage characteristics of light-emitting devices based on a close-packed layer of CdTe quantum dots and on CdTe/polymer (polyaniline or polypyrrole) composites.

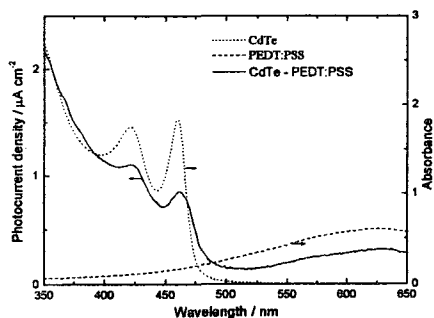


Figure 3. Absorption spectra of thin films of CdTe nanocrystals and PEDT:PSS compared with a photocurrent action spectrum of the composite CdTe/PEDT:PSS film (measured in a 0.1 M solution of $(\text{C}_4\text{H}_9)_4\text{NBF}_4$ in acetonitrile containing 0.01 M hydroquinone (electrode potential -0.7 V).

colloidal solutions both by wet chemical aqueous synthesis and by a recently developed organometallic route using mixtures of highly boiling primary amines and trioctylphosphine as the size-regulating and coordinating solvents. Procedures of solvent exchange, surface modification, and functionalization of nanocrystals

Another approach to form nanocrystal/conducting polymer composites was the use of mixtures of aqueous colloids of CdTe quantum dots with anionic poly (3,4-ethylenedioxy-thiophene):poly (4-styrenesulphonate) complex (PEDT:PSS). Thin film composites prepared from these solutions by spin-coating were studied by means of electro- and photoelectrochemical methods. The photocurrent spectra (Fig. 3) and photocurrent-potential curves indicate an efficient exchange of photogenerated charges between the quantum dots and the polymer matrix. The as-prepared highly doped composite CdTe/PEDT:PSS films can be electrochemically reduced to a range of doping levels permitting a better match between the band edges of the quantum dots and the polymer matrix.

CdTe nanocrystals synthesized in aqueous solutions were used to form luminescing shells on monodisperse latex spheres by applying the layer-by-layer deposition technique of polyelectrolytes and quantum dots [4]. The luminescing composite core-shell spheres were further used as building blocks to prepare 3D colloidal photonic crystals shown in Fig. 4. The influence of the photonic bandgap on the spontaneous emission of quantum dots is currently under investigation.

In conclusion, highly luminescing CdSe, CdTe, CdHgTe and HgTe quantum dots were prepared in

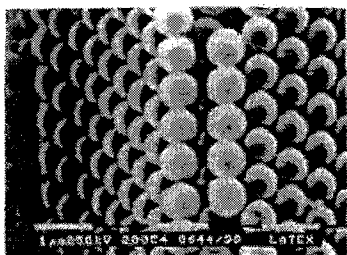


Figure 4. Scanning electron microscopy image of a 3D colloidal photonic crystal prepared from composite latex/CdTe spheres.

nanocrystals in polyaniline, polypyrrole and in a complex of poly (3,4-ethylenedioxythiophene)-poly (4-styrenesulphonate) have been studied. 3D colloidal photonic crystals have been prepared from monodisperse latex spheres with luminescing CdTe shells.

This work has been partially supported by the research grant INTAS-Belarus 97-250 and the NATO Collaborative Linkage Grant CLG 976365.

References

1. Eychmüller A., Rogach A. L., *Pure Appl. Chem.* **72** (2000) 179.
2. Kershaw S. V., Harrison M., Rogach A. L., Kornowski A., *IEEE J. Select. Topics Quant. Electr.* **6** (2000) 534.
3. Gaponik N. P., Talapin D. V., Rogach A. L., Eychmüller A., *J. Mater. Chem.* **10** (2000) 2163.
4. Rogach A. L., Sussha A. S., Caruso F., Sukhorukov G. B., Kornowski A., Kershaw S., Möhwald H., Eychmüller A., Weller H., *Adv. Mater.* **12** (2000) 333.

FAST ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FOR NANOCHEMISTRY AND NANOPHYSICS

G. A. RAGOISHA, A. S. BONDARENKO

*Physico-Chemical Research Institute, Belarusian State University
Minsk 220080, Belarus*

E-mail: ragoisha@fhp.bsu.unibel.by

Fast electrochemical impedance spectroscopy technique has been developed for *in situ* simultaneous investigation of the AC frequency and DC potential dependence of the nanostructures impedance and their electrochemical transformations monitoring. The technique based on the time domain analysis of the response to the digitally generated multi-frequency excitation provides the real-time three-dimensional data visualization in Windows and does not require any additional software.

1 Conventional electrochemical impedance spectroscopy

Electrochemistry provides material science with a lot of useful techniques both for investigation of the microheterogeneous systems [1] and preparation of nanostructured materials [2]. The direct application of the electrochemical technique for nanoparticle characterization is based on the dependence of the redox potential and other thermodynamic characteristics on electronic structure. The variation in particle size results in the outer electron shell energy changes that can be revealed by the electrochemical experiment using potentiometry and voltammetry [3]. Immediate measurements of the size-dependent thermodynamic characteristics, however, are not always feasible. Therefore the electrochemical technique usually derives the information indirectly from measurements of the kinetic characteristics dependent on the electronic structure of a nanostructured electrode.

Electrochemical impedance spectroscopy (EIS) [4] is one of the most powerful electrochemical techniques. Unlike the DC voltammetry, EIS can be used for the nondestructive investigation of the solid-liquid interface as it analyses the response to very low-amplitude (≤ 10 mV) AC probing signal superimposed on the DC bias. The AC response is usually informative even in the blank potential region of the DC voltammetry. The EIS derives information from the amplitude of the AC current and the phase shift between current and potential considered as functions of the AC frequency and DC bias. The AC response at a constant DC potential is commonly represented as a set of Nyquist plots (dependence of the imaginary impedance component on the real part on the complex impedance plane) and Bode plots (frequency dependencies of the phase shift and the impedance magnitude). Fig. 1 shows such plots for the simplest electrochemical cell that is represented by the

electric capacitance of the solid-liquid interface. The semicircle on the Nyquist plot results from the frequency dependence of the AC impedance of the capacitor. The capacitance of the metal-liquid interface results from the charged double layer on the metal surface, while the capacitance of the semiconductor electrode is due to the series of two capacitive elements - the double layer in the liquid phase and the depletion-layer in the semiconductor. Both capacitances are size dependent. Dielectric nanoparticles distort the electric double layer on the electrode surface and thus can be also detected by their effect on the double-layer capacitance. Besides the capacitive elements, the equivalent electric circuit of the nanostructured electrode comprises of the ohmic resistance attributed to the charge transfer, and the specific elements attributed to the diffusion. In the case of a flat electrode with semi-infinite linear diffusion the diffusion contribution to the impedance is represented by the Warburg element that has a constant -45° phase shift and the magnitude inversely proportional to $\omega^{1/2}$, while the nanostructured systems show more complex behaviour that has not been sufficiently investigated because of the limitations of conventional EIS techniques.

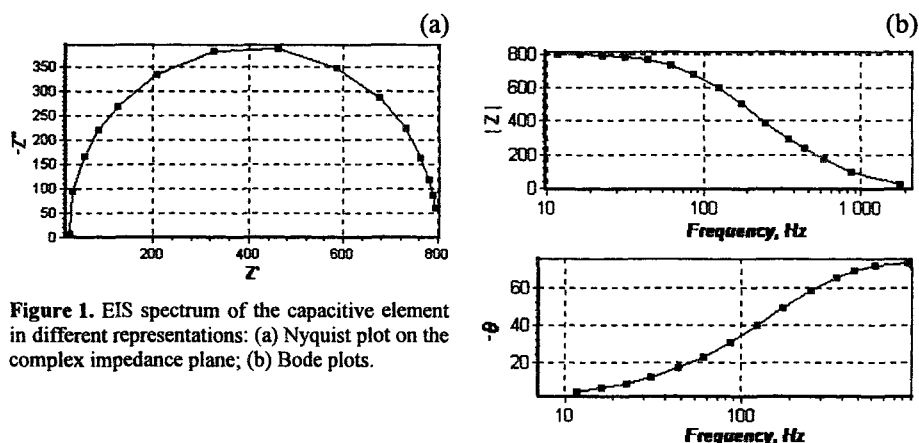


Figure 1. EIS spectrum of the capacitive element in different representations: (a) Nyquist plot on the complex impedance plane; (b) Bode plots.

The analysis of the EIS data is based on the different frequency and DC potential dependence of the impedance components [4]. In order to allow the quantitative analysis, the impedance spectra must be obtained fast enough to have a consistent data sets in the frequency and the DC bias dependencies. The low speed of the common EIS techniques makes the main problem for the EIS method for nanostructured materials.

The most noticeable advancement in EIS for the non-stationary systems was made with the Fourier transform instrumentation [5]. The Fourier transform EIS eliminates the AC frequency scanning by the use of the multi-frequency excitations followed by the conversion of a response signal from the time domain to the frequency domain with the Fourier transform. The latter can be fast but it has some

drawbacks. First, the response of the electrochemical system depends on the frequencies sequence in the probe. Therefore, an EIS signal in the frequency domain contains the sequence-dependent components that drastically complicate the data analysis. Second, EIS has a low sensitivity resulting from the excitation energy distribution in a wide frequency range. This can be partially fixed up by application of the probing signal in several 'bursts', each one containing a fraction of the whole number of frequencies [5]. The side effect of this solution is obviously the extension of the measurement duration.

2 Fast EIS

The concept of our approach to the fast EIS (FEIS) grounds on the digital AC probing in the real-time system [6] that was specially designed for the automation of the fast computerised electrochemical measurement and control under the Windows environment. The real-time system [6] provides the direct hardware control with 0.5-1 microsecond precision using conventional ISA-extension analog-to-digital and digital-to-analog conversion boards. Due to the real-time digital probing, the probe and the response use the same accurate time scale, which allows the EIS data analysis in the time domain. The high accuracy of the time scale compensates for the inevitable losses in accuracy of electric current measurement that result from the low-amplitude confinement of the probe signal.

The trick of the high-accuracy current measurement in our technique is in the substitution of the amplitude measurement by calculation of the amplitude from the real-time regression analysis of the response time series. Thus, the accuracy of current measurements increases with the time series length and can be efficiently controlled. The regression analysis assumes that the response to the sine probe is also a sine. The validity of this assumption in the case of the non-linear system is provided by very low amplitude of the probe (≤ 10 mV).

The surmounting of the frequency scan overheads is also a result of the programing trick. The AC probe is composed from the sequence of the sine waves of different frequency joined in the train in a way that minimises the transient processes attributed to the frequency tuning. In order to eliminate the frequency tuning transients completely, several front waves in each frequency are excluded from the analysis. The pre-scanning mode of the program gives possibility to optimise the required number of the wave periods in each frequency and the number of periods to be excluded from analysis. The AC wave trains are applied sequentially at every step of the potentiostatically controlled DC potential. The DC potential scan rate is controlled by the height and duration of the DC step.

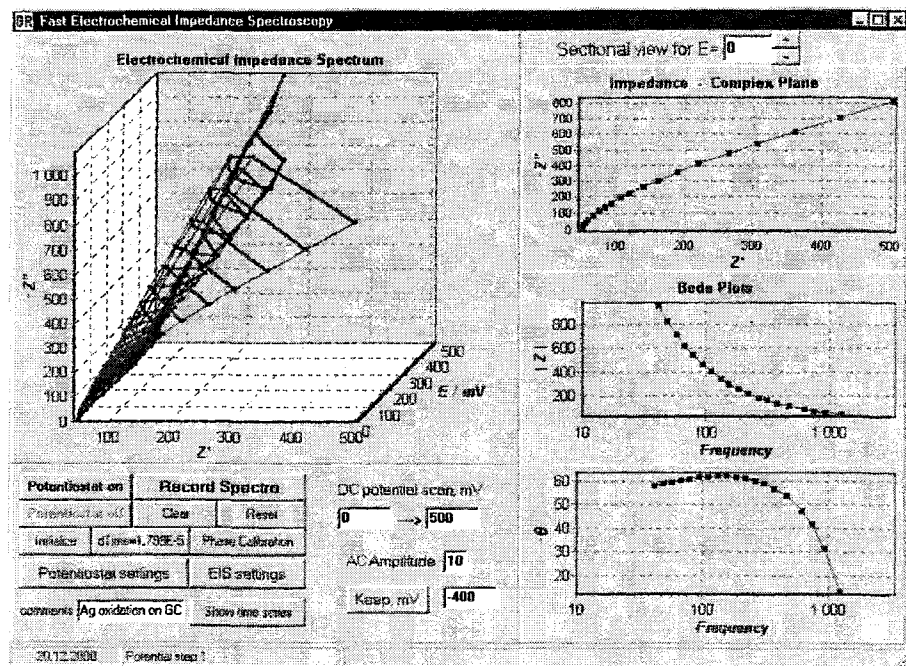


Figure 2. The FEIS screenshot monitoring the anodic oxidation of Ag nanoparticles on the glassy carbon electrode surface.

The processor resources free from the potentiostat control and data acquisition are used in the real-time analysis and plotting. Fig. 2 shows a FEIS screenshot for nanoparticle electrochemical transformation. The plots on the right side of the screen that are similar to the common representation of EIS data (Nyquist and Bode plots) appear repeatedly during the DC potential scanning. The three-dimensional plot of the DC potential dependence of the impedance spectra appears on the left side. The constant potential sections of the three-dimensional FEIS spectrum can be re-plotted after the experiment using the up-down button control above the Nyquist plot. The above-mentioned real-time plotting requires a fast processor (we used 450 MHz Pentium III).

Thus, we have developed the FEIS technique for *in situ* simultaneous investigation of the AC frequency and DC potential dependence of impedance of nanostructures and monitoring their electrochemical transformations.

3 Acknowledgements

This work was supported in part by research grant INTAS-Belarus 97-250.

References

1. Cottis R. A. Llewellyn A. M., *Electrochemical Techniques* (UMIST, 1996), available at http://www.cp.umist.ac.uk/lecturenotes/Echem/index_main.htm.
2. Rogach A. L., Kotov N. A., Koktysh D. S., Ostrander W., Ragoisha G. A., Electrophoretic Deposition of Latex-Based 3D Colloidal Photonic Crystals: A Technique for Rapid Production of High-Quality Opals, *Chem. Mater.* **12** (2000) pp. 2721-2726.
3. Ragoisha G. A., Surface structures on non-metallic electrodes, catalysts of the oscillating anodic reactions, *Surf. Sci.* **331-333** (1995) pp. 300-305.
4. MacDonald J. R., *Impedance Spectroscopy* (John Wiley & Sons, N.Y., 1987).
5. Schiewe J., Hazi J., Vicente-Beckett V. A., Bond A. M., A unified approach to trace analysis and evaluation of electrode kinetics with fast Fourier transform electrochemical instrumentation, *J. Electroanal. Chem.* **451** (1998) pp. 129-138.
6. Ragoisha G. A., Data acquisition and control in a user-mode real-time system for electrochemical equipment automation, *Dedicated Systems Magazine* (2000, Quarter 2) pp. 33-36.

KINETICS OF TIP INDUCED OXIDATION BY SCANNING PROBE MICROSCOPE

S. A. GAVRILOV, S. V. LEMESHKO, V. I. SHEVYAKOV

*State Research Physical Problems Institute
103460 Moscow, Russia*

V. M. ROSCHIN

*Moscow Institute of Electronic Engineering
103498 Moscow, Russia*

E-mail: pcfme@dpts.miee.ru

It is shown that the tip induced oxidation process can be considered as an electrochemical anodic oxidation. The model of the oxidation kinetics is proposed. It is shown that film resistance, relative humidity, applied voltage and duration of oxidation influence the rate and spatial resolution of the process. The formation of 8 nm oxide patterns by tip induced oxidation is demonstrated.

1 Introduction

The progress in scanning probe microscopy (SPM) transforms scanning tunnelling microscope (STM) and atomic force microscope (AFM) from measuring devices into the nanotechnological tool. The demonstration of single electron transistor fabrication by nanooxidation [1] opens perspectives to develop an industrial nanolithography processing. However, an absence of detailed understanding of tip induced oxidation mechanism limits this process integration in nanotechnology.

The results of numerous works shows that electrical and structural properties of the positive biased surface are changed unreversible in air at room temperature by the tip effect. The common explanation of these changes is an oxide formation. Dependences of the oxide lines and hillocks dimensions on conditions of the tip induced treatment obtained in various studies allow to propose an electrochemical mechanism of the nanooxidation. The abrupt dependence of oxidation rate on humidity observed in [2] confirms the roll of adsorbed electrolyte (water) layer in the nanooxidation. This fact is in a good agreement with the electrochemical model. However, there are other parameters affecting the oxidation rate, e.g., the electrical conductivity of an oxidized material [3].

In present paper on the basis of classical electrochemistry we consider a conductive AFM tip induced oxidation of a Ti film deposited on SiO₂. Experimental data and parameters of the process predicted theoretically allow us to find some analogy between the tip induced oxidation in air and the anodic oxidation in aqueous solutions.

2 Results and discussion

Nanolithography was performed on Ti films, as thin as 2 ± 1 and 8 ± 1 nm, evaporated by a cathode arc deposition technique on the thermally oxidized silicon substrate. The continuous amorphous films had surface roughness of about 0.1 nm.

The commercial SPM P47 SOLVER (NT-MDT Co. Russia, Zelenograd) was used for the tip induced oxidation. The silicon cantilevers (Silicon-MDT) covered by W_2C were used as probes for nanolithography. The tip induced oxidation was carried out in the tapping mode of AFM. The experiments were made in air. The humidity around AFM was about 60 %. During oxidation the tip was negatively biased respect to a sample. The bias voltage was varied from 0 to 10 V. The duration of voltage supply was varied from 1 to 16 ms.

The typical surface morphology of Ti film after the tip induced treatment at negative tip bias is shown in Fig. 1. An appreciable morphology change is only observed if the sample bias value was higher than 6 V. The maximum increase of the film thickness was 1.6 and 5.0 nm for Ti films of 2 nm and 8 nm thickness, respectively. These changes may be prescribed to TiO_2 formation. It follows from the difference between density of Ti and TiO_2 .

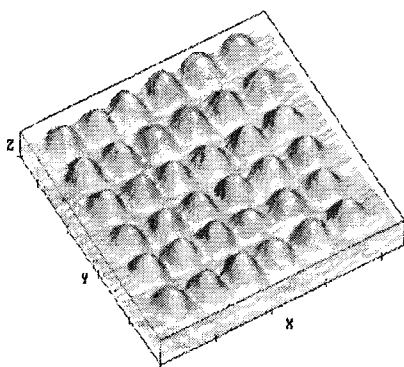


Figure 1. AFM image of the nanodot array formed by tip induced oxidation on Ti surface.

To explain the observed phenomena we have proposed an electrochemical mechanism of oxidation. Experimental dependences of oxide pattern heights vs applied voltage and oxide heights vs anodization duration are presented in Fig. 2. The obtained results appear to be in some contradiction with the parameters of anodic oxidation. Namely, the non-linear shape of the obtained relationships occurs. However, the use of electrochemical laws can give a proper insight.

Kinetics of any electrochemical process may be expressed in terms of the Faraday law:

$$h_{ox}(t) = \frac{\eta Q A_{ox}}{S \rho_{ox} z F} = \frac{\eta \chi}{S} \int_0^t J(t) dt, \quad \chi = \frac{A_{ox}}{\rho_{ox} z F}, \quad (1)$$

where A_{ox} is the molar mass of the oxide, ρ_{ox} is the oxide density, S is the area of oxidized surface, F is the Faraday constant, Q is the charge consumed for oxidation, $J(t)$ is the anodic current, η is the current efficiency, i.e. the part of total current that consumed for oxidation, z is the number of electrons that takes part in oxidation.

Under potentiostatic oxidation the bias voltage (U) is distributed between the growing oxide (U_{ox}) and the electrochemical circuit that consist of an electrolyte, a substrate and interconnections (U_c). Thus we can write

$$U = U_c + U_{ox} = J(t) R_c + E h_{ox}(t), \quad (2)$$

where R_c is the electrical resistance of the circuit, E means an electric intensity, that activates ion transport trough the oxide during anodic film formation.

According to (1) and (2), the measured change of oxide thickness during anodization (Δh_{ox}) may be defined as follows

$$\Delta h_{ox}(t) = k \frac{U}{E} \left(1 - \exp \left(- \frac{E \chi}{R_c S} t \right) \right), \quad (3)$$

where k is a factor that takes into account the difference between volumes of the oxide and consumed metal.

The resistance effect upon the oxidation rate describes the non-linear dependence of h_{ox} vs U under the same duration of the anodic treatment. Namely, the higher metal film resistance or lower thickness of the film results in the lower oxide growth rate (Fig. 2).

This model allows us to predict a width of the oxide pattern. The parameter R_c includes a resistance of adsorbed water layer too. This resistance increases with the water layer thickness. Therefore the pattern width is to be increased with increasing relative humidity. This proposition is in agreement with the experimental results of the work [2]. On the other hand, if the oxidation duration is too long the anodic oxide growth must be observed at the some distance from the tip. If the oxide thickness reaches a maximum value near the tip, an anodic current starts to flow through the neighboring regions. Therefore, at shorter pulses or higher scan rates the tip induced oxidation can result in the higher spatial resolution. Such a dependence of oxide width on the scan rate was observed in numerous works [1-3].

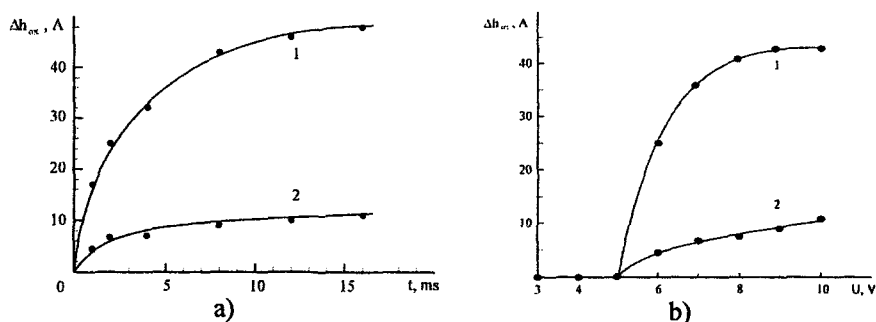


Figure 2. Experimental dependences of oxide pattern height vs oxidation time at 10 V (a) and vs applied voltage for 10 ms (b) measured after the tip induced oxidation of 8 and 2 nm Ti film (curves 1 and 2, respectively).

According to this model, an enhancement of nanooxidation resolution may be achieved by increasing of metal film thickness and decreasing of oxidation duration at an optimum voltage. The local surface oxidation of thick Ti films (15 nm) was made: the shorter oxidation time (0.5 ms) with bias voltage 8 V results in the oxide line with minimum line width of 8 nm.

In conclusion, the proposed model allows us to define an optimum regimes of the nanooxidation for formation of large arrays of oxide patterns with minimum time expenses.

References

1. Matsumoto K., Room temperature operated single electron transistor made by STM/AFM nano-oxidation process, *Physica B* **227** (1996) pp. 92-94.
2. Held R., Heinzel T., Studerus P., Ensslin K., Nanolithography by local anodic oxidation of metal films using an atomic force microscope, *Physica E* **2** (1998) pp. 748-752.
3. Workman R. K., Peterson C. A., Sarid D., Current-dependent growth of silicon nitride lines using a conducting tip AFM, *Surf. Sci.* **423** (1999) pp. L277-L279.

FEATURES OF LUMINESCENT SEMICONDUCTOR NANOWIRE ARRAY FORMATION BY ELECTRODEPOSITION INTO POROUS ALUMINA

S. A. GAVRILOV, D. A. KRAVTCHENKO

*Moscow Institute of Electronic Engineering
Zelenograd, 103498 Moscow, Russia*

A. I. BELOGOROKHOV

*Institute of Rare Metals
Leninsky Prospect 156-517, 117571 Moscow, Russia*

E. A. ZHUKOV, L. I. BELOGOROKHOVA

*Moscow State University, Physics Department
Moscow, Russia*

E-mail: pcfme@dpts.miee.ru

Technological conditions for electrodeposition of luminescent CdS into porous anodic alumina are determined on the basis of calculation of thermodynamic equilibria in the CdS-H₂O electrochemical system. A potential-pH diagram of CdSO₄-Na₂S₂O₃-H₂O solution is used to determine the deposition mechanism. Possibility of CdSe and ZnSe nanowire fabrication into nanopores is demonstrated.

1 Introduction

Optical properties of semiconductor nanostructures attract a great interest because of possibility to create new optoelectronic devices. A^{II}B^{VI} compound semiconductors are widely used for that. The demonstration of successful synthesis of CdS nanowire arrays by electrodeposition into pores of anodic alumina [1] opened new prospects in this direction. It is well known that electronic properties of semiconductors depend on structure and composition of the material. Therefore detailed understanding of processes occurred during electrodeposition is necessary to control physical properties of the structures.

CdS electrodeposition mechanism is expressed often by the reaction [2]



However this reaction can not describe the observed relationship of the deposited film composition vs pH and concentration of the electrolyte.

In this paper a potential-pH diagram is used for prediction of CdS electrodeposition mechanism. We show that pH and solution concentration effect the Cd/S ratio in the deposited film. Using the diagram we find optimum

technological conditions for formation of CdS nanowire arrays into pores of anodic alumina. An analogous approach allowed us to fabricate luminescent CdSe and ZnSe nanowire arrays into pores of porous anodic alumina and porous silicon.

2 Theoretical analysis

Potential-pH diagrams are widely used for prediction of mechanisms of various electrochemical processes [3]. We have calculated electrochemical equilibrium in the $\text{CdSO}_4\text{-Na}_2\text{S}_2\text{O}_3\text{-H}_2\text{O}$ system.

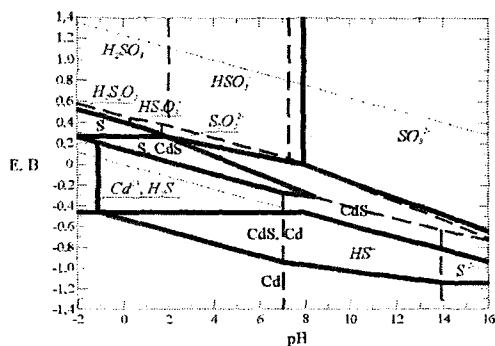


Figure 1. Potential-pH diagram of $\text{CdSO}_4\text{-Na}_2\text{S}_2\text{O}_3\text{-H}_2\text{O}$ electrochemical system.

according to the cathode potential, S is the first deposited substance in acidic media, CdS is the second, and Cd is the third one. In the range of pH from 2 to 8, the CdS deposition precedes the S deposition. And in alkaline media S deposition is impossible.

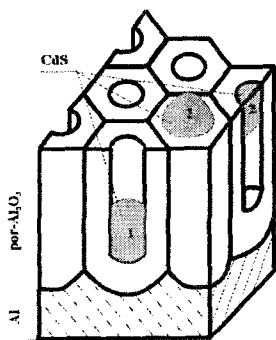
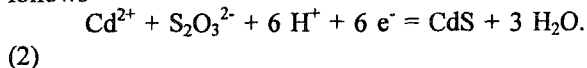
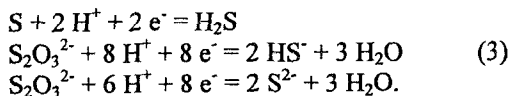


Figure 2. Schematic presentation of nanowire formation (1) and encapsulation of pores (2).

The results of calculations show that in acidic media ($-2 < \text{pH} < 2$) CdS deposition occurs according to the reaction (1). In more alkaline media the CdS electrochemical formation can be described as follows



At high cathode potentials the deposition of CdS results from chemical interaction between Cd^{2+} and H_2S , HS^- , or S^{2-} via following reactions



Such chemical interaction results in compound formation in the bulk of the solution. This process may be accompanied with encapsulation of pore entrances, and nanowire formation becomes impossible

(Fig. 2). To prevent closing of the pores it is necessary to use potentials or current densities, and pH of the solution maintaining predominance of the reaction (2).

3 Results and discussion

An aluminum foil of 10 μm thickness was used as a substrate for preparation of porous anodic alumina (PAA). It was performed in 10 % H_2SO_4 aqueous solution at 1 mA/cm^2 for 1 h at room temperature. The AFM measurements showed that average pore diameter was about 10 nm. Depth of PAA was about 0.6 μm .

CdS was deposited into PAA from an aqueous solution of 10 mM CdSO_4 and 5 mM $\text{Na}_2\text{S}_2\text{O}_3$ at different pH. The pH was varied by addition of H_2SO_4 or NH_4OH . After the deposition CdS films were annealed in air at 500 $^\circ\text{C}$ during 1 h.

Cyclic voltammetry (CVA) was used to investigate kinetics of the electrodeposition. CVA was performed in the three-electrode cell at 10 mV/s sweep rate. Saturated calomel electrode was used as a reference electrode. Two Pt plates with the area of 2 cm^2 were used as working and opposite electrodes for CVA measurements.

The performed CVA measurements allowed us to detect a sequence of the cathode reactions occurred in the investigated system. The potentials of the registered reactions were in agreement with the values estimated from the diagram. On the basis of experimental data we selected the regimes of CdS nanowire arrays deposition into PAA. The cathode deposition was performed at -0.5 V (vs. saturated calomel electrode) from the aqueous solution containing 0.01 M CdSO_4 and 0.01

$\text{Na}_2\text{S}_2\text{O}_3$ at pH = 5-7. This optimum regime allowed us to fill nanopores of Al_2O_3 by the CdS nanowires.

The luminescence spectrum of CdS crystallized in pores of Al_2O_3 (broad band with maximum at 2.65 eV) was blue-shifted to the visible spectral region compared with that of the bulk CdS (Fig. 3). This energy shift allowed us to estimate the average size of nanostructures: the radius is about 4.9 nm. In this case the dielectric confinement of excitons in semiconductor quantum wires restricted by the dielectric medium has been taken into account [4]. Obtained sizes coincided with the results of AFM measurements. Results of FTIR spectroscopy of the samples had peaks of LO and TO phonons and confirmed the

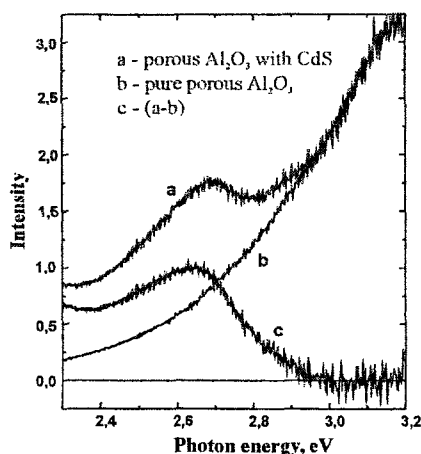


Figure 3. Photoluminescence spectra of CdS nanowires in PAA.

CdS nanocrystal formation. It is necessary to note that CdS nanowires formed under other conditions of deposition had a broad red-shifted luminescence. This red-shift was explained by the excess of S and Cd in the films deposited in acidic and alkaline media, respectively. Similar results were obtained at high cathode potentials.

In conclusion, the electrochemical equilibrium diagram allows to find optimum regimes of CdS deposition into nanometer pores. A composition of the deposited material can be controlled by pH and concentration of the solution. The approach developed opens the pathway of fabrication of luminescent CdSe and ZnSe nanowire arrays in pores of anodic alumina and porous silicon.

4 Acknowledgements

This work was supported by the RFBR (Grants Nos. 99-02-18327 and 97-02-17600) and by the program "Physics of Solid-State Nanostructures" (Grant 97-1083 and 97-102).

References

1. Routkevitch D., Bigioni T., Moskovits M., Xu J. M., Electrochemical fabrication of CdS nanowire arrays in porous anodic aluminium oxide, *J. Chem. Phys.* **100** (1996) pp. 14037-14047.
2. Goto F., Ichimura M., Arai E., A new technique of compound semiconductor deposition from an aqueous solution by photochemical reactions, *Jpn. J. Appl. Phys.* **36** (1997) pp. L1146-L1149.
3. Pourbaix M., *Atlas of Electrochemical Equilibria in Aqueous Solutions* (National Association of Corrosion Engineers, Houston, 1974).
4. Gavrilov S. A., Gusev V. V., Dneprovskii V. S., Zhukov E. A., Syrnikov A. N., Yaminskii I. V., Muljarov E. A., Optical properties of excitons in CdS semiconductor-insulator quantum wires, *JETP Lett.* **70** (1999) pp. 216-221.

STRUCTURAL, ELECTRICAL AND GAS SENSING PROPERTIES OF COPPER PHTHALOCYANINE NANOPARTICLES IN POLYSTYRENE

A. V. MISEVICH, A. E. POCHTENNY, I. P. ILYUSHONOK

*Belarussian State University of Technology
Sverdlova Street 13a, 220050 Minsk, Belarus*

E-mail: root@bstu.unibel.by

O. M. STUKALOV

*Institute of Solid State and Semiconductor Physics, National Academy of Sciences of Belarus
P. Browka Street 17, 220072 Minsk, Belarus*

E-mail: nanom@iftf.bas-net.by

Thin films of copper phthalocyanine (CuPc) – polystyrene (PS) composites were prepared by laser evaporation in vacuum. The crystalline structure of CuPc nanoparticles and composite film morphology were investigated by TEM, AFM and optical absorption method in relation with DC electrical conduction and adsorption-resistive response to NO₂.

1 Introduction

CuPc compounds are of great interest as chemical sensors [1]. The dispersion of CuPc in polymer medium increases the surface-volume ratio of active phthalocyanine particles and can improve a CuPc response to gas adsorption. The aim of this work is to perform comparative study of crystalline structure, morphology, DC dark electrical conduction and adsorption-resistive response to NO₂ of CuPc–PS composite thin films depending on different CuPc content, film thickness and heat treatment conditions.

2 Experiments

The CuPc–PS composite films with thickness of 10–200 nm were prepared by a LGN-703 CO₂ laser evaporation in vacuum of 10⁻³ Pa. Targets were pressed tablets of CuPc and PS mixture. The evaporated products were co-deposited on NaCl, glass, mica and polycore substrates at room temperature.

The optical properties of CuPc nanoaggregates and morphology of CuPc–PS films were investigated using SPECORD-M40 spectrophotometer, EM-125 K transmission electron microscope, and Nanoscope IIIa AFM.

The DC dark electrical conduction of composite films with different concentrations of adsorbed oxygen was measured at 290–420 K by the high speed cooling method [2] using V7-49 electrometer. The adsorption-resistive response to 2 ppm NO₂ in air was measured under the dynamic mode at 330–470 K. To investigate the influence of annealing on film structure, morphology and properties, the samples were annealed in air and vacuum at temperatures up to 520 K.

3 Results and discussion

It is a well known [1], that CuPc has two crystalline modifications – metastable α -phase and stable β -phase. The visible spectra of both α - and β -phases have a double peak absorption band with the peak wavelength at 615 and 694 nm for α -phase and 645 and 712 nm for β -phase. Visible spectra show that all laser deposited CuPc-PS composite films were crystallized in α -phase. The annealing in air and vacuum at temperatures up to 520 K does not change the CuPc crystalline structure. Fig. 1 shows a typical visible spectrum of CuPc-PS composite films.

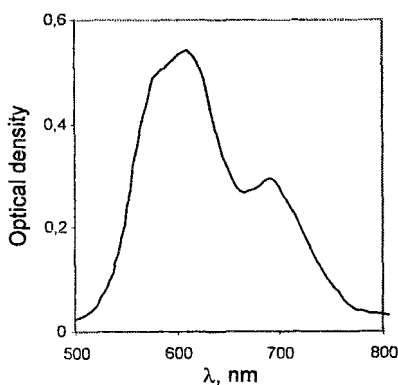


Figure 1. Absorption spectrum of 10 % CuPc-PS composite film.

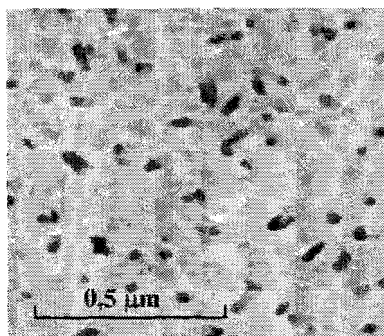


Figure 2. TEM micrograph of 20 % CuPc-PS composite film after annealing in air at 470 K.

Both TEM and AFM show (Figs. 2, 3) that the CuPc is dispersed in PS matrix as nanoparticles with size, changing with temperature and environment of annealing. Surface morphology of deposited CuPc-PS composite films does not visualize crystallites, phase interfaces or other structure features (Fig. 3, left). Annealing in air at temperatures below 470 K for 1h does not change significantly the film morphology. Annealing in air above 470 K causes recrystallization of CuPc in the films with formation of needle-like crystallites of 150–200 nm in length and of 40–60 nm in width (Fig. 3, right). Annealing in vacuum at 470 K leads to the formation of grain morphology in film surface with grains of 50–70 nm. In both

cases phase interfaces are not visualized, hence, film surface contains only CuPc crystallites.

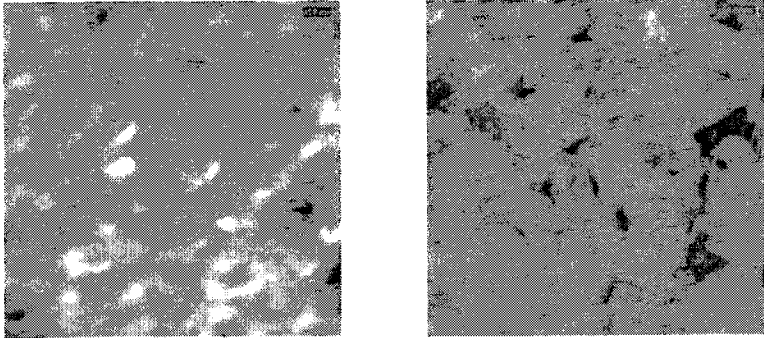


Figure 3. AFM images of deposited 20 % CuPc–PS composite film of 100 nm (left) and the same film after annealing in air at 470 K (right). Image size 1 μm .

Thus, the CuPc–PS composite films are amorphous polystyrene media containing dispersed α -phase CuPc nanoparticles. Polymer softening during the annealing can initiate recrystallization of CuPc.

It is known that CuPc has a hopping conduction mechanism [2,3]. Therefore, the dependence of conduction G on temperature T can be expressed as

$$G = G_0 \exp(-E_a/kT), \quad (1)$$

with the tunnel factor [2]

$$G_0 = G_{03} \exp[-(4\pi/3)^{1/3} \alpha e^2 / \epsilon a E_a], \quad (2)$$

where E_a is the activation energy, k is the Boltzmann constant, α is the percolation constant, e is the electron charge, ϵ is the dielectric constant, a is the electron radius of localization.

Fig. 4 shows a typical set of conduction temperature dependencies which were obtained for different concentrations of adsorbed oxygen. Every line gives a value of G_0 and E_a for constant oxygen concentration (1). The set of measured G_0 and E_a for different oxygen concentrations gives a linear $\ln G_0 - 1/E_a$ plot (Fig. 5).

The electron transport in CuPc films occurs in accordance to (2) via states with electron radius of localization 0.27 nm. Oxygen desorption can increase the concentration of localization centers. Therefore, adsorbed oxygen molecules block electron transport centers. Concentration of localization centers in CuPc–PS during the oxygen desorption increases at the beginning, afterwards it decreases. This fact shows that the transition from impurity to intrinsic electron transport states during oxygen desorption occurs with decreasing of electron radius of localization from 0.072 nm to 0.047 nm, which are significantly less in comparison to CuPc films due to reducing of intermolecular interaction.

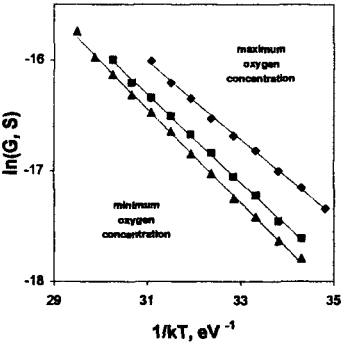


Figure 4. Temperature dependencies of 2 % CuPc-PS film conductance at three different oxygen concentrations.

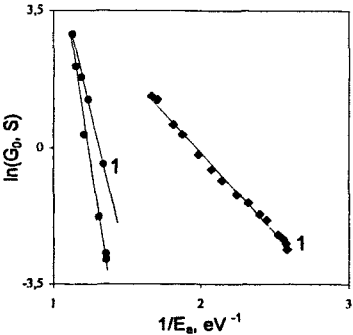


Figure 5. Experimental data for CuPc (right) and 20 % CuPc-PS (left). Points 1 correspond to maximum oxygen concentration.

Fig. 6 shows the kinetics of relative sensitivity S with respect to NO_2 for CuPc-PS composite films after annealing at different temperatures. S is a ratio of film conductance in presence of NO_2 to conductance in air. S decreases during annealing process accordingly with crystallization of CuPc. Fig. 7 shows the dependence of S on the concentration of CuPc in evaporated target. The composite film formed from the 20 % CuPc-PS target has maximum adsorption-resistive response to NO_2 and minimum times of response and recovery.

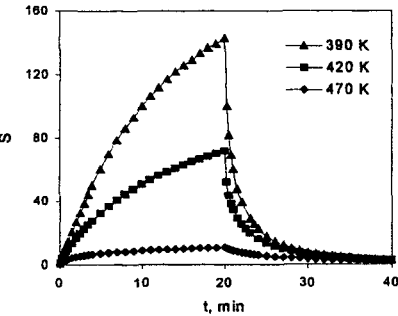


Figure 6. The relative response to 2 ppm NO_2 of 2 % CuPc-PS composite at 390 K after annealing.

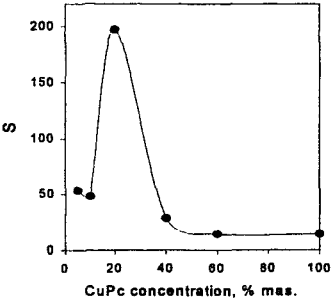


Figure 7. The dependence of relative response to 2 ppm NO_2 of CuPc-PS composite films on concentration of CuPc in evaporated target.

In conclusion, laser co-evaporation of CuPc and PS allows to prepare thin films containing CuPc nanoparticles in PS matrix. The hopping conduction in the films is

realized through intrinsic or adsorbed oxygen electron states. CuPc-PS films can be used as chemical gas sensors with enhanced sensitivity and time response.

References

1. Wright J. D., Gas adsorption and conductivity of phthalocyanines, *Progr. Surf. Sci.* **31** (1989) pp. 1-60.
2. Pochtenny A. E., Sagaidak D. I., Fedoruk G. G., Misevich A. V., Hopping conduction in copper phthalocyanine and its polymer composites, *Phys. Sol. State* **38** (1996) pp. 1422-1426.
3. Misevich A. V., Pochtenny A. E., The effect of gas adsorption on hopping conduction in metallophthalocyanines, *Electron. Technol.* **33** (2000) pp.167-170.

This page is intentionally left blank

NANOTECHNOLOGY

This page is intentionally left blank

MICRO- AND NANOSTRUCTURES: PREPARATION AND APPLICATIONS

R. KASSING

*Institute of Mikrostructure Technologies and Analytics (IMA), University of Kassel
Heinrich-Plett-Str. 40, D-34132 Kassel, Germany*

E-mail: Kassing@physik.uni-kassel.de

Micro- and nanostructures are of exponentially creasing importance in our information community. The realisation of those structures makes use of the very successful technology used already for microelectronics, i.e. corresponding material and microstructuring processes (lithography and etching). The combination of these technologies to quite new devices, complex systems, i.e. MEMS and MOEMS is the great challenge. The paper presents our results mainly obtained in realising complex sensors for scanning probe microscopy [1-9].

1 Introduction

In our global society, communication and information transfer is playing a role of exponentially increasing importance. This means that there is always a need for increased, faster information transfer. Since the velocity of the information transfer is limited by the speed of light, the only real strategy for improved throughput is to make the distance and in turn the physical structures smaller. This need for ever increasing information processing speeds has driven the ever decreasing structure sizes applied in microelectronics. A new challenge exists, namely to exploit the very successful microelectronics technology to create and realize quite new devices and entirely new micro- and nanosystems.

There are a number of technological and material problems hindering the proliferation of these small systems. Nanometer-scale structures which actuate or act over a short, sub-picosecond period demand a better understanding of material properties on these same scales and therefore necessitate the development of new material evaluation schemes. Based on this improved understanding of essentially molecular scale material properties, drastic improvements and quite new materials may be realized, and from this new technological possibilities and even smaller structures can be developed. This would necessitate further refinement in material understanding, in essentially a self-sustaining iterative process.

To realize smaller structures, they must be written in a sensitive resist and then transferred into the corresponding substrate. Therefore, one must always deal with lithography and dry etching problems. In this paper, we will concentrate on the

main problems of lithography and dry-etching and present new applications in the form of micro- and nanosystems used as sensors for scanning probe microscopy.

2 Lithography

In Fig. 1, the *International Technology Road map for Semiconductors (ITRS)* is shown, which defines the dimensions of future devices, guiding interested companies in their development efforts. It can be seen that structures below 100 nm are predicted within a few years, in fact the Pentium III from Intel already uses 130 nm structures and achieves a 733 MHz maximum frequency. Standard optical lithography will no longer allow reductions in the structure size, because the diffraction limit is approximately the wavelength, λ , obviating the need for next generation lithography (so-called NGL) development. Extreme UV (or EUV) and Ion Projection Lithography (IPL) are believed to be the most promising NGL technologies.

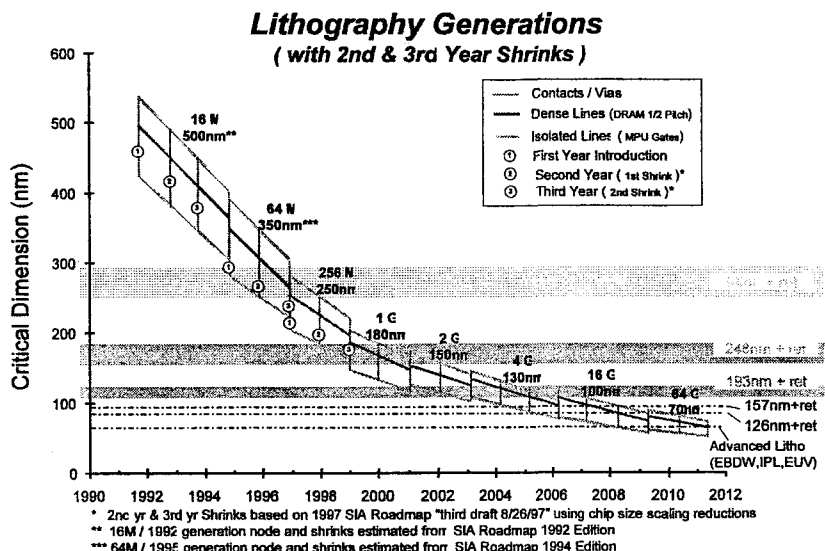


Figure 1. The International Technology Road map for Semiconductors (ITRS).

In IPL, around 100 keV He^+ or H^+ ions of a multi-cusp-ion source are passed through several electromagnetic lenses and a so-called open stencil mask which contains the pattern to be transferred to the resist on top of the wafer. The structures on the mask are four times larger than those transferred onto the resist on the wafer because the optics of the system reduces the figure size by a factor of 4. The energy distribution of the ions is kept smaller than 1 eV.

One of the biggest problems in developing this complex system is mask preparation, and is only discussed briefly here. Fig. 2 shows the principle of the mask making process.

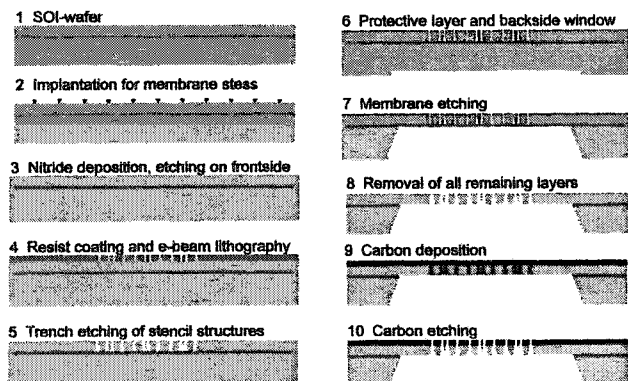


Figure 2. The principle of the mask making process.

institute. Since the wavelength, λ , of the 100 keV H^+ ions is around 10^{-5} nm, the ion wavelength does not define the resolution in IPL, instead the resolution is defined by the interaction of the ions with the material. Therefore, a numerical aperture of 10^{-5} is possible, yielding the largest imaging area of all lithographic techniques, which is a decisive advantage of IPL.

Fig. 3 shows the first 200 mm diameter mask containing structures of 200 nm, which due to the reduction of the optics of IPL results in 50 nm structures on the wafer.

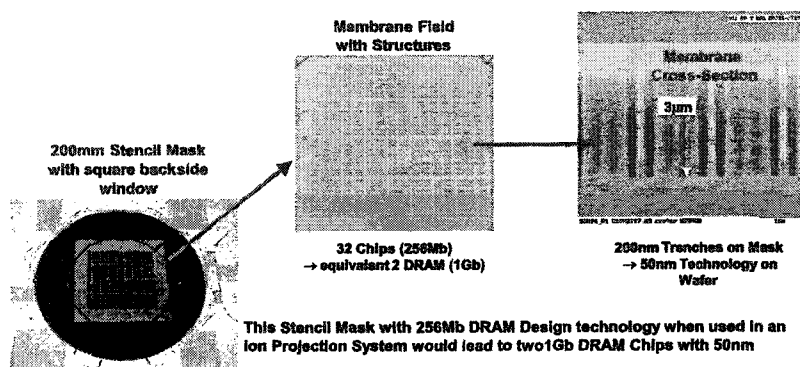


Figure 3. First 200 mm IPL mask containing structures of 200 nm, thus yielding 50 nm structures on the wafer.

A silicon on insulator (referred to as SOI) wafer of up to 200 mm diameter is thinned by wet etching to obtain a $3\ \mu\text{m}$ membrane using the oxide layer as an etch stop. The necessary structures are etched by a special plasma etching process using the gas chopping technique developed at our

2.1 Dry etching

After transferring the mask structures onto the wafer resist through lithography, these structures in turn must be transferred into the substrate. Due to the extremely

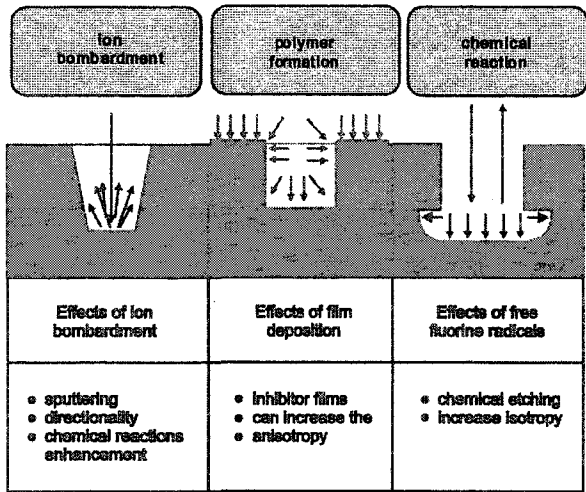


Figure 4. Basic physical and chemical phenomena in plasma - solid interaction.

small structures involved, only plasma etching is plausible for accurate pattern transfer. The basic principle of dry etching is that in a plasma, activated gas particles, neutrals or ions, impinge onto and react with the substrate, producing volatile products which can be pumped away. Fig. 4 illustrates the principles involved.

Ion bombardment yields a high directionality (but a small selectivity), and energy-dependent low etch rate and an energy-dependent defect

production rate. Pure chemical reactions yield a higher possible etch rate and selectivity, but due to the spontaneous etching, yields a nearly isotropic etch behavior. To achieve simultaneous high etch rates, high selectivity, low defect production and high directionality (vertically etched walls), there are two manufacturing strategies available:

1. Apply side wall protection using the gas-chopping technique discussed above.
2. Etching under low temperatures, with kT small compared with the chemical activation energy, so that no spontaneous reaction can take place.

Fig. 5 shows the effect of side wall protection in the gas-chopping technique. In (a), pure fluorine gas is used to plasma etch the substrate, yielding the isotropic profile. In (b) and (c), increasing the content of a polymer forming gas (CH_3F) allows production of vertical walls but also a reduced etch rate because the deposited film needs to be removed.

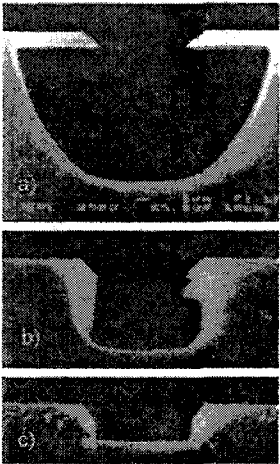


Figure 5. The effect of side wall protection in the gas-chopping technique.

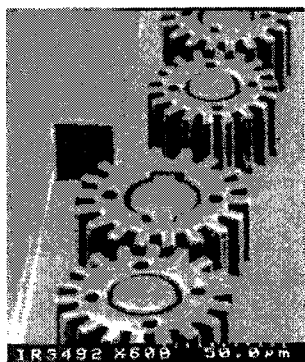


Figure 6. Results of low temperature etching without side wall protection.

Fig. 6 shows the results of low temperature etching without side wall protection. To achieve these structures, the material aspect ratio must be taken into account. Fig. 7a, b illustrate a common difficulty - if the material ($7\ \mu\text{m}$ carbon in this case) is not stress free, one may obtain the result shown.

However, if all of these factors are considered, successful MEMS like the micro-gripper shown in Fig. 8 can be realized.

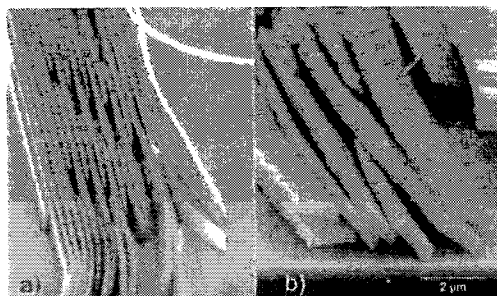


Figure 7. Influence of non optimal material properties (stress) during dry etching.

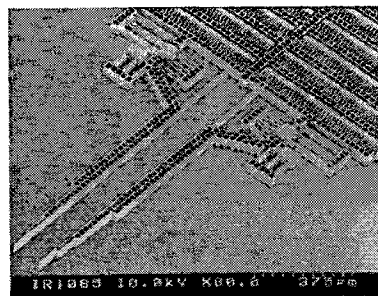


Figure 8. Micro-gripper.

3 Sensors for Scanning Probe Microscopy (SPM)

Combining lithography, etching techniques and corresponding materials allows realization of quite new and exciting micro- and nanosystems. Innovative sensors for SPM are the application considered here. The intent is to develop probes which are able to detect material properties with high lateral resolution, and if possible, with sub-picosecond response. This should allow electrical, mechanical, optical, thermal and chemical properties of surfaces to be determined at relevant length and time scales.

Fig. 9 shows the general principle of scanning force microscopy (SFM): a cantilever containing a sharp tip at its end is scanned over the surface of a sample by an actuator system. The interaction of the tip with the sample results in bending of the cantilever in contact mode or, in the case of dynamic or tapping mode, in a change in the resonance curve of the cantilever's vibration. These effects are

detected by a beam deflection method or using a piezoresistive detection system (Fig. 9).

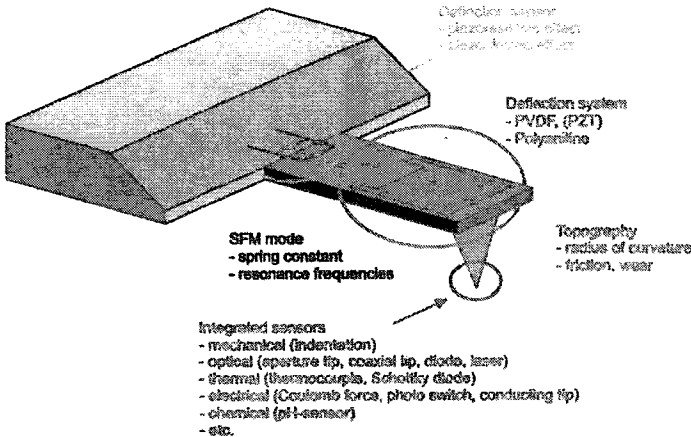


Figure 9. The general principle of scanning probe microscopy (SPM).

The cantilever tip plays the decisive role; a modified tip will allow the measurement of electrical, mechanical, thermal, optical or chemical material properties. In the following discussion, the piezoresistive detection system and some selected probe types will be discussed.

3.1 Piezoresistive detection

Fig. 10 shows a cantilever with a Wheatstone bridge of piezoresistors.

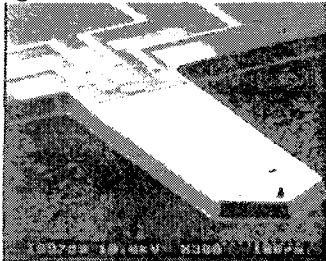


Figure 10. Cantilever with a Wheatstone bridge of piezoresistors.

Applying a mechanical stress to a silicon cantilever, through bending for example, changes its surface area and its electrical resistance occur. The system shown has a longitudinal and transversal effect with the corresponding piezoresistive constants π_l and π_t , respectively. With the mechanical stress components σ_l and σ_t , one obtains

$$\left(\frac{\Delta R}{R}\right)_l = \pi_l \sigma_l \text{ and } \left(\frac{\Delta R}{R}\right)_t = \pi_t \sigma_t \text{ with } \pi_l \approx \pi_t = \pi.$$

This results in

$$\frac{\Delta R}{R} = \pi \frac{3Et}{2l^2} z = \pi \frac{6l}{wt^2} F,$$

where l , w , and t are the length, width and thickness of the cantilever, respectively, E is the elastic modulus, z is the bending distance and F is the applied force.

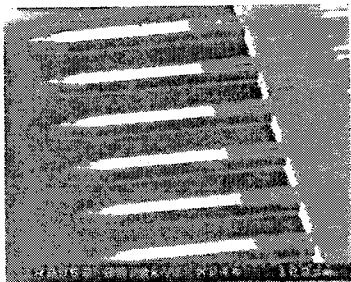


Figure 11. Array of silicon cantilevers for atomic force microscopy (AFM) applications.

The sensitivity of this system can be modified by these parameters. Fig. 11 shows an array of silicon cantilevers for atomic force microscopy (AFM) applications making use of this piezoresistive detector system.

A hole has been placed at the clamped end of the cantilever which has been shown by the finite element calculations to increase the sensitivity. If the hole size is increased, one obtains the structure shown in Fig. 12, which permits to detect lateral forces.

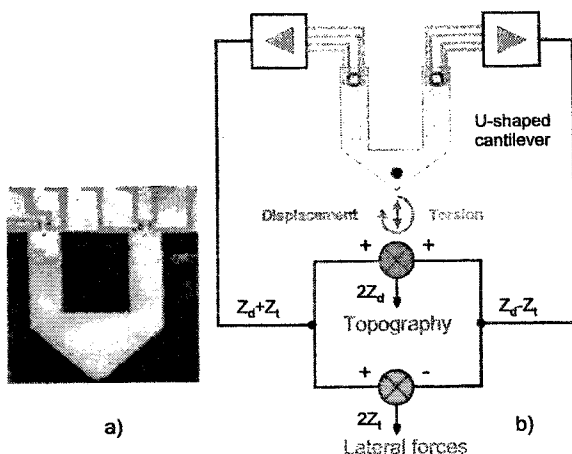


Figure 12. Cantilever for detection of lateral forces, where a) shows the probe and b) outlines the measuring principle.

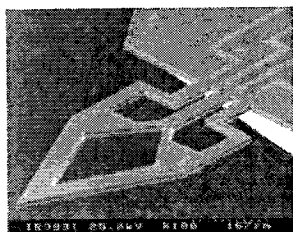


Figure 13. A more complex cantilever with additional detection possibilities.

The two Wheatstone bridges of the system allow measurement of a homogeneous bending of the two arms, as well as any torsion in the cantilever by a difference in the bending of the two arms. An even more complex system is shown in Fig. 13, where in addition to bending and torsion of the cantilever, an obstruction to the tip can be detected.

The same type of cantilevers with a piezoresistive detection system can be used for chemical sensors. Fig. 14 shows a high-sensitivity cantilever and piezoresistor system with an additional resistive heating element.

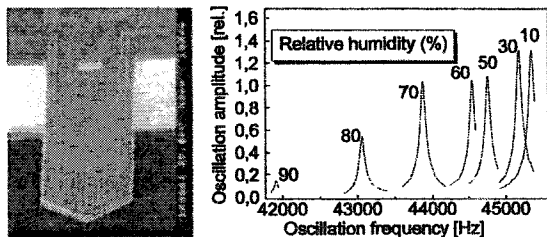


Figure 14. Microheater covered with moisture-sensitive polymer working as a hygrometer.

A polymer film is placed on top of the heating element which should be detected by high sensitivity and high lateral resolution, i.e., only several molecular layers are necessary to change the resonance curve of the mechanical system. In Fig. 14 an example of results using moisture-sensitive polymers is shown.

4 Scanning Nearfield Optical Microscopy (SNOM)-Sensors

The lateral resolution of optical microscopy is determined by the scattering effect. Using the so-called Rayleigh criterium the resolution limit δ is defined by

$$\delta = \lambda / (n \sin \alpha),$$

where λ is the wavelength and $n \sin \alpha$ is the numerical aperture. To overcome this limit, scanning optical nearfield microscopy (SNOM) is used (Fig. 15).

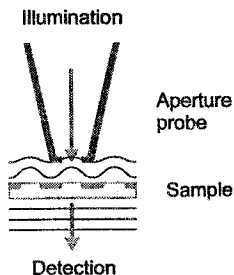


Figure 15. The principle of scanning optical nearfield microscopy (SNOM).

A cantilever with a hollow tip is scanned over the surface of the sample under test and the light of a laser shines into the hollow of the tip. The diameter of the hollow tip aperture is much smaller (30-100 nm) than the wavelength λ of the laser light. Inside the hollow tip the light at some point reaches an area with a diameter equal to the wavelength of the light. In this area most of the intensity of the light is totally reflected and only a small amount of the light is emitted in form of an evanescent wave from the small aperture. This evanescent wave is used to characterize optical properties of the sample. Therefore the distance between aperture and sample surface has to be very small. In this method the size of the aperture determines the lateral resolution, as opposed to the wavelength. The main technological problem is to produce hundreds of these SNOM sensors on a silicon wafer with uniform aperture sizes, with the sizes ranging from 30 nm to about 100 nm. Fig. 16 presents a SNOM-sensor showing an aperture of about 45 nm, Fig. 17 presents the result of a measurement of a sample with structures in the same order.

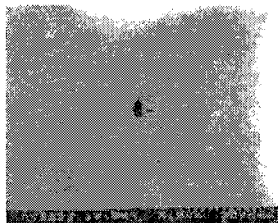


Figure 16. SNOM-sensor showing an aperture of about 45 nm.

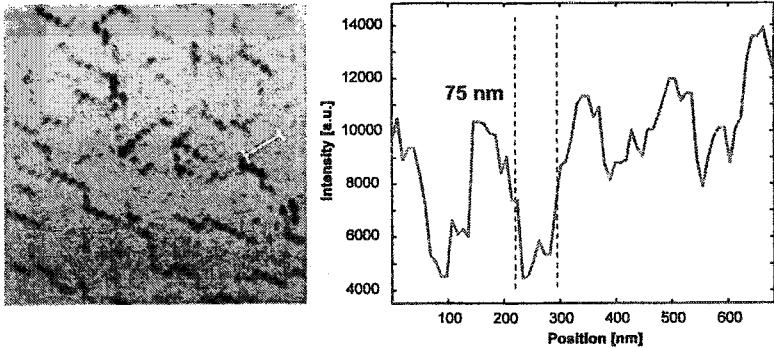


Figure 17. The result of a measurement on a “Fischer-Sample”.



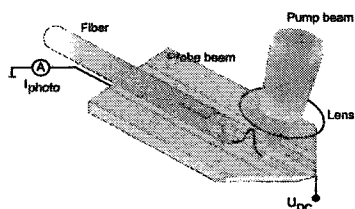
Figure 18. GaAs-cantilever showing the tip as well as the VCSEL.

This type of SNOM-sensor needs an external laser for illumination. However, it is also possible to use an integral laser. A vertically emitting laser, a so-called VCSEL, can be used in the aperture. Because such a laser cannot be realised in silicon, GaAs is used as a cantilever and tip material. Fig. 18 shows the realised sensor where the tip as well as the VCSEL can be seen.

5 Sensors for high lateral and highest time resolution

All the sensors described so far show a high lateral resolution. But there is great interest to combine simultaneously high lateral with high time resolution, especially in microelectronics, where electrical signals with high lateral resolution have to be measured at high frequencies or very short periods. Standard sampling techniques are unable to show neither the high lateral nor time and frequency resolution. To measure in the high frequency mode, sensors (cantilevers with tip) covered with a corresponding coplanar line are realised and scanned over the device with the small structures under test. If the frequency of the signal in the device is ω_m that of the sensor is chosen as $\omega t = \omega_m + \Delta\omega$, with $\Delta\omega$ to be equal to the mechanical resonance frequency of the cantilever. Therefore, if the device under test is working, i.e. showing the signal with frequency ω_m , the cantilever (sensor) is oscillating with its mechanical resonance frequency, otherwise it is not. This has been tested so far up to about 40 GHz in collaborative work with the University of Duisburg.

Measurements in the time domain are more complicated. To this purpose we developed an extreme fast photo-switch in a GaAs-cantilever (Figs. 19, 20).



Cross correlation measurement

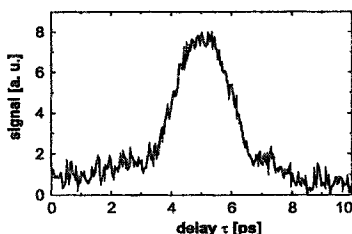


Figure 19. Illustration of the principle of the photo-switch.

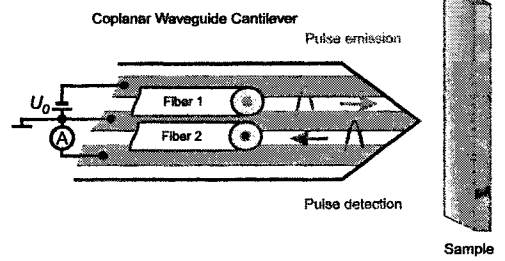


Figure 21. The principle of scanning nearfield microwave microscopy (SNMM).

detected by a second coplanar line. Therefore the material properties of the sample can be detected.

6 Summary

The need for smaller structures – especially in microelectronics – drives the synergistic combination of physics and technology. For the realization of such small structures, material and technological (lithography, dry etching) problems have to be solved. If smaller structures can be realized, quite new devices – micro- and nanosystems – can be developed. Scanning probe microscopy (SPM) makes use of this effect. This allows a much better microscopic understanding of material and technological problems, thus even smaller structures may be realized – a circular process.

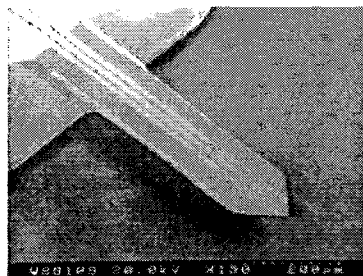


Figure 20. The realization of the photo-switch.

A 100 fs laser pulses through an optical fiber creating enough electron-hole pairs in the GaAs to produce a short-cut between the conducting lines, which results in an electrical pulse in the range of 500 fs if the material and coplanar line is chosen correctly.

By this method these very short pulses can not only be created but also detected, thus a high time resolved electrical material characterisation should be possible.

Following the SNOM idea, by this method a scanning nearfield microwave microscope (SNMM) can be realized, as illustrated in Fig. 21.

The photo-switch realizes the short pulse which will be reflected, influenced by the sample and

7 Acknowledgements

I would like to thank my leading coworkers Dr. Egbert Oesterschulze, Dr. Ivo Rangelow and Dr. Wenzel Scholz for their support. The DFG, BMBF and the Ministry of Science of Hesse I have to thank for their financial support.

References

1. Kassing R., Oesterschulze E., Sensors for scanning probe microscopy. In *Micro/Nanotribology and Its Application*, ed. by Bharat Bushan (Kluwer Academic Publisher, 1997) pp. 35-54.
2. Mihalcea C., Scholz W., Werner S., Münster S., Oesterschulze E., Kassing R., Multi-purpose sensor tips for scanning nearfield microscopy, *Appl. Phys. Lett.* **25** (1996) pp. 3531-3533.
3. Kulisch W., Malaveé A., Lippold G., Mihalcea C., Oesterschulze E., Fabrication of integrated diamond cantilevers with tips for SPM, *Appl. Diamond. Relat. Mater.* **6** (1997) pp. 906-911.
4. Werner S., Münster S., Heisig S., Mihalcea C., Scholz W., Oesterschulze E., Application and characterization of combined SNOM/SFM cantilever probes, In *SPIE 3009-09* (1997) pp. 130-140.
5. E. Oesterschulze, O. Rudow, C. Mihalcea, W. Scholz, Werner S., Cantilever Probes for SNOM applications and double aperture tips, *Ultramicroscopy* **71** (1998) pp. 85-92.
6. Oesterschulze E., Kassing R., Thermal and electrical imaging of surface properties with high lateral resolution. In *Proceedings of the 16-th International Conference on Thermoelectrics* (Dresden, IEEE, 1997) pp. 719-725.
7. Heisig S., Oesterschulze E., Gallium arsenide probes for scanning near-field probe microscopy, *Appl. Phys. A* **66** (1998) pp. 385-390.
8. Leinhos T., Stopka M., Oesterschulze E., Micromachined fabrication of Si cantilevers with Schottky diodes integrated in the tip, *Appl. Phys. A* **66** (1998) pp. 65-69.
9. Vollkopf A., Rudow O., Oesterschulze E., Kassing R., Eggers G., Fumagalli P., Rosenberger A., Güntherodt G., Microfabricated aperture probes for polarization sensitive scanning nearfield optical microscopy, submitted to *J. Vac. Sci. Technol.*, 1999.

MASSIVELY PARALLEL ATOMIC LINES ON SILICON CARBIDE

P. SOUKIASSIAN

*Commissariat à l'Energie Atomique, DSM-DRECAM-SPCSI-SIMA
Bâtiment 462, Saclay, 91191 Gif sur Yvette Cedex, France
and*

*Département de Physique, Université de Paris-Sud
91405 Orsay Cedex, France*

E-mail: psoukiassian@cea.fr

The atomic scale ordering and properties of cubic silicon carbide surfaces are investigated by room and high temperature scanning tunneling microscopy. In this review, I focus on the Si-terminated β -SiC(100) surfaces only. Self-formation of Si atomic lines and dimer vacancy chains on the β -SiC(100) surface is taking place at the phase transition between the 3×2 (Si rich) and $c(4\times 2)$ surface reconstructions. Using a rigorous protocol in surface preparation, it is possible to build very long, very straight and defect free Si atomic lines, forming a very large superlattice of massively parallel lines. These self-organized atomic lines are driven by stress. They have unprecedented characteristics with the highest thermal stability ever achieved for nanostructures on a surface (900 °C) and the longest atomic lines ever built on a surface (μm scale long). Investigating their dynamics, we learn that their dismantling at high temperature results from collective and individual mechanisms including one-by-one dimer removal. Overall, this is a model system especially suitable in nanophysics and nanotechnologies.

1 Introduction and historical background

Silicon carbide (SiC) is certainly not a new material since it is older than the solar system. Indeed, SiC has been discovered in 1895 by Henri Moisan (1904 Chemistry Nobel Prize laureate) on a meteorite located in the Diablo Canyon (Arizona) [1]. Initially, silicon carbide has been established for its excellent mechanical properties as "carborundum" since it was primarily used for many decades as a hard material (the highest hardness after those of diamond and boron nitride). SiC now became very well known as an advanced material having many versatile and promising applications in e.g. matrix composites, biocompatibility or microelectronics [2-4]. In the latter field, SiC appears to be especially suitable for high-power, high-temperature, high voltage, high frequency and radiation resistant electronic devices and sensors [2-4]. Its average figures of merit scale up to 3 orders of magnitude above those of conventional semiconductors such as Si or III-V compounds, SiC being outclassed only by diamond [5-10]. Fig. 1 shows the representative figures of merit of various conventional and novel semiconductors according to the criteria established by Keyes (high speed logic and high integration density electronic

devices) [5] and by Johnson (high power, high speed, high temperature and high voltage analogic devices) [6].

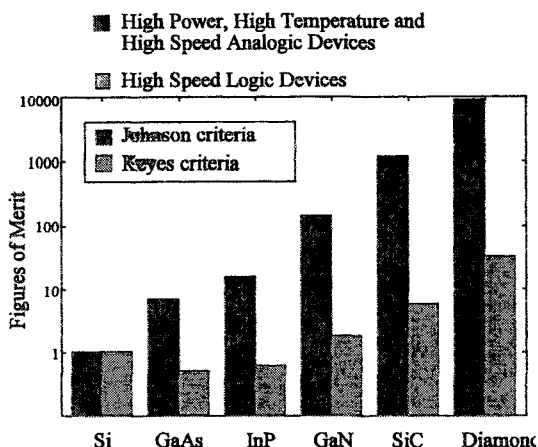


Figure 1. Figures of merit of various semiconductors according to the criteria of Keyes [5] (high speed logic devices) and Johnson [6] (high power, high temperature and high speed analogic devices).

Furthermore, SiC is chemically rather inert which, combined with its excellent ability to resist to radiation damages, makes it a very suitable material for harsh environments [2,9]. Also, SiC is a "refractory" IV-IV compound semiconducting material belonging to the class of wide band gap semiconductors (together with diamond and group III nitrides) and a very high thermal stability [2-4]. This makes it very useful for operations at elevated temperatures ($\geq 600^\circ\text{C}$ to 800°C instead of $< 150^\circ\text{C}$ e.g. for silicon) [2-9]. Overall, these characteristics give to SiC many potential applications in aerospace, automotive, electronics and nuclear industries [2-9]. In addition, due to a small mismatch in lattice parameters, SiC (in both cubic and hexagonal phases) is a very suitable substrate for III-V nitride epitaxial growth [2]. SiC exists in (β) cubic, (α) hexagonal (more than 170 polytypes) or rhomboedric crystallographic phases, having band gaps ranging from 2.4 eV to 3.3 eV which could potentially allow to make homojunctions and superlattices based on the same material [11]. Its breakdown field, thermal conductance, band gap and saturated drift velocity are respectively $\times 10$ times, $\times 3$ times (same as Cu), $\times 2$ times and $\times 2$ times higher than silicon [2-4].

Unlike other group IV semiconductors, SiC is not a fully covalent semiconductor with a significant charge transfer between C and Si, which could give polar surfaces. With the availability of good quality samples, the understanding and control of both cubic and hexagonal SiC surfaces and interfaces has been successfully achieved only recently, contrary to conventional semiconductors [2]. Cubic SiC has the zinc blende structure with alternating Si and C planes, leading for β -SiC(100) to many different surface reconstructions ranging from Si-rich 3×2 , 8×2 ,

5x2, 7x2, 9x2,, Si-terminated c(4x2) and 2x1, C-terminated c(2x2) and C-rich 1x1 graphitic surfaces, as evidenced by both experimental and theoretical investigations [2,8,12-33]. Due to very large mismatches between lattice parameters when comparing β -SiC(100) with Si(100) (- 20 %) and C(100) (+ 22 %), the Si surface plane is under very large compressive stress while the C surface plane would be, in turn, under strong extensive stress [2,8,12-20,30,33]. This makes SiC as a test case to probe the effect of stress on surface organization. Indeed, these effects are dominant features in β -SiC(100) surface ordering such as for the c(4x2) reconstruction. Based on scanning tunneling microscopy (STM) experiments and core level photoemission spectroscopy, we have shown that the β -SiC(100) c(4x2) surface reconstruction results from Si-Si dimer rows having alternating up- and down-dimers (AUDD model) within the row [15,22]. This very particular surface ordering has not been observed for any other surface and results from a large surface stress as already indicated above [6,7,10,12,17]. The AUDD model is further supported by *ab-initio* total energy calculations [30,31]. We should remark that the behavior of the β -SiC(100) surface is very different from corresponding Si(100), Ge(100) and C(100) surface reconstructions. The central issue is the control, at the atomic scale, of SiC surfaces and interfaces. In addition to high quality well defined surfaces, interesting features such as a semiconducting c(4x2) to metallic 2x1 phase transition has been discovered [24] with evidence of a non-Fermi liquid behavior [33]. Interestingly, at the phase transition between Si-rich and Si-terminated β -SiC(100) surfaces, the self-organized formation of highly stable Si atomic lines has been observed [8,9,13,16,19,23,33]. In addition, for the C-terminated surface [17,18,21], a temperature-induced sp to sp^3 diamond-type transformation has also been discovered with the formation of sp^3 carbon atomic lines [20]. Such C atomic lines could cover the all surface leading to a surface terminated by carbon atoms in a sp^3 configuration [20]. This finding could potentially be very useful in providing a substrate for single crystal diamond growth [9].

In this review, I present some of these latest investigations on the control and understanding, at the atomic level, of Si atomic lines and atomic vacancy chains that are self-organized on cubic β -SiC(100) surfaces. These studies are primarily based on STM experiments. Such important issues as the atomic structure, the role of stress in surface ordering and self-organized Si nanostructures are presented. These Si atomic lines have unprecedented characteristics such as unprecedented thermal stability (> 900 °C) and lengths (> 1 μ m) making them potentially very useful in nanotechnology.

2 Experimental details

The STM experiments are performed using room temperature and variable temperature scanning tunneling microscopes (RT-STM and VT-STM) operating in

ultra high vacuum conditions. The pressure in the experimental and preparation chambers is always kept in the very low 10^{-11} Torr range. We use single crystal, single domain β -SiC thin films (about $1\ \mu\text{m}$ thick) prepared at CEA-LETI (Grenoble), at the Laboratoire de Multimatériaux et Interfaces, Université Claude Bernard (Lyon) or at Centre de Recherche sur l'Hétéroépitaxie, CNRS (Sophia Antipolis) by C_3H_8 and SiH_4 chemical vapor deposition (CVD) growth on vicinal (4°) Si(100) wafers. Very high quality Si-terminated β -SiC(100) 3×2 and $c(4\times 2)$ surface reconstructions can be routinely prepared from sequences of thermal annealing and Si deposition. This procedure is shown to result in very reproducible and clean surfaces as confirmed by sharp single domain low energy electron diffraction (LEED) patterns and specific electronic surface states in the valence band photomission spectra. The control of the various β -SiC(100) surface reconstructions has been achieved by core level and valence band photoemission spectroscopies using synchrotron radiation at the Synchrotron Radiation Center (SRC, Madison, Wisconsin, USA), Advanced Light Source (ALS, Berkeley, USA), Synchrotron Radiation Research Center (SRRC, Hsinchu, Taiwan) and Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France). Other experimental details about high quality SiC surface preparation could be found elsewhere [8,12-16,19,33-38].

3 Massively parallel atomic Si lines and Si dimer chain vacancies on the β -SiC(100) surface

The actual trend in microelectronics is towards much higher integration densities with a road map suggesting a doubling every 18 months (Moore law). However, some serious limitations in this downsizing approach are rising for the near future raising very fundamental questions. Another approach would be to manufacture desired patterns by assembling atoms one-by-one using e.g. STM manipulations [39,40]. However, such methods require very long processing times to achieve nanostructures having the desired properties and, to limit surface diffusion, low temperatures. This means that, as soon as the surface is warmed-up e.g. at room temperature, atom surface diffusion will destroyed the obtained nanopatterning. As adequately mentioned in the White House National Nanotechnology Initiative [41], there are some important questions such as i) "what new and novel properties will be enabled by nanostructures, especially at room temperature ?", ii) "what are the surface reconstructions and atoms rearrangement in nanorods and nanocrystals ?", iii) "can one use extensively self-assembly techniques to control nanoscale component relative arrangements ?".

It is interesting to correlate these questions to the recent discovery, at the phase transition between the Si-rich 3×2 and Si-terminated $c(4\times 2)$ reconstructions of the β -SiC(100) surface the self-organized formation, upon temperature-induced β -SiC(100) 3×2 surface dismantling, of Si atomic lines having unprecedented

characteristics - see Fig. 2 - [8,9,13,16,19,23,33,38]. They are: i) very long with a length limited by the substrate only, ii) very stable, iii) made of Si-Si dimer lines, iv) the density/spacing of these Si atomic lines could be mediated by a single process, thermal annealing, resulting in arrangements ranging from a single isolated Si line to a superlattice of "massively parallel" Si atomic chains [8,9,13,16,19,23,33,38]. At the very beginning of the β -SiC(100)3x2 surface dismantling, one can see in Fig. 3a that the Si atoms are removed dimer row by dimer row, leaving very long Si dimer vacancy leaving very long Si dimer vacancy chains on a 3x2 surface reconstruction [37]. Using a very rigorous protocol in surface preparation, we can now prepare defect free Si dimer lines as shown in a representative STM topograph (Fig. 3(b)) [37].



Figure 2. Si atomic lines on β -SiC(100) surfaces. 800 Å x 800 Å STM topographs (filled electronic states) of β -SiC(100) surfaces after annealing: a) Si atomic lines forming a superlattice of massively parallel atomic lines after annealing at 1050 °C; b) Si atomic lines obtained after annealing at 1100 °C; c) isolated single Si atomic line on the β -SiC(100) c(4x2) surface after annealing at 1150 °C. The two top atomic lines are separated by 400 Å.

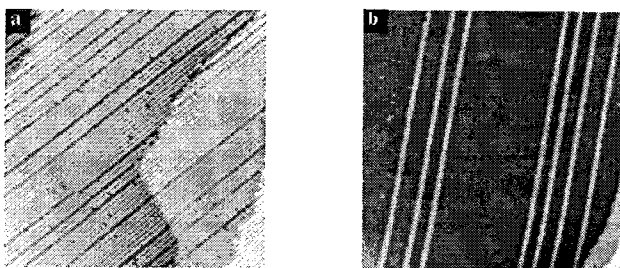


Figure 3. a) Si dimer vacancy chains on the on β -SiC(100) 3x2 surface. 525 Å x 525 Å STM topographs (filled electronic states) of β -SiC(100) 3x2 surface reconstruction exhibiting dimer row vacancies after a short annealing at 1050 °C. b) Si dimer lines on a β -SiC(100) c(4x2) surface: 800 Å x 800 Å STM topograph. Notice the quality of these lines that are defect free or almost defect free.

In order to identify the atom position in these lines, it is necessary to image the surface by tunneling into the empty electronic states. To correlate filled and empty topographs, we also perform dual scan STM imaging. Fig. 4(a,b) provide a comparison between empty and filled electronic state topographs of the same atomic lines [37]. One can clearly see in the empty state topograph that, by tunneling into Si dangling bonds, the lines are made of pairs of atoms forming the

Si-Si dimers observed in the filled state topograph [37]. Fig. 4(c) displays the corresponding height profile along a dimer in the empty electronic state STM topographs. One can clearly notice that the Si-Si dimer is symmetric [37], unlike the corresponding behavior of the 3×2 surface reconstruction, where dimer forming rows are asymmetric [8,14,19]. This indicates that, when the 3×2 surface is dismantled by thermal removal of Si atoms, the spacing between dimer rows increases thereby significantly reducing the lateral interaction [37].

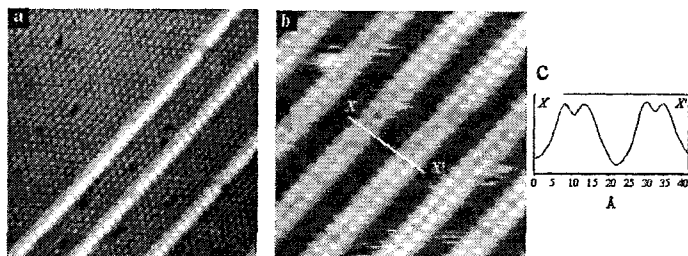


Figure 4. Identification of the Si atom positions for Si atomic lines: a) Filled electronic states $125 \text{ Å} \times 125 \text{ Å}$ STM topograph showing the Si-Si dimers forming atomic lines on the β -SiC(100) $c(4 \times 2)$ surface. b) $125 \text{ Å} \times 125 \text{ Å}$ STM topographs (empty electronic states) showing the Si atoms forming the atomic lines. c) Height profile along XX' showing the symmetric nature of the Si-Si dimers.

Another possible interesting ordering configuration is to have these atomic lines self assembling by pairs in a very particular 8×2 surface array that are imaged by filled and empty STM topographs in Fig. 5(a,b), respectively, with a joint height profile in Fig. 5(c) [23]. A height profile also shows that the dimers are already symmetric [23]. This particular 8×2 array is taking place at the phase transition between the 3×2 (Si-rich) and the 5×2 (equidistant Si atomic lines) surface reconstructions.

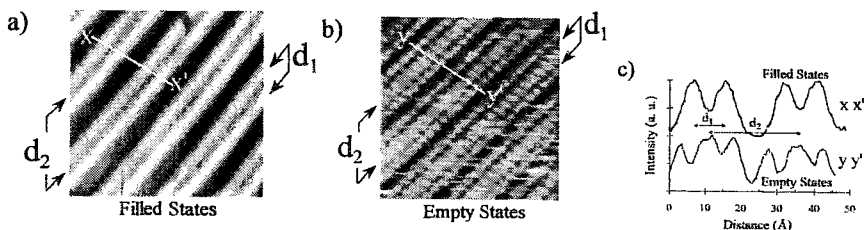


Figure 5. Pairs of Si atomic lines on β -SiC(100) forming a 8×2 surface reconstruction: a) $100 \text{ Å} \times 100 \text{ Å}$ filled electronic state STM topograph. The intra-pair distance d_1 represents the lateral row-to-row distance within an atomic lines. The inter-pair distance d_2 represents the distance between the centers of two neighboring atomic lines. b) $100 \text{ Å} \times 100 \text{ Å}$ empty states STM topograph with d_1 and d_2 same as in a). Note overlap between dangling bonds from two adjacent Si atoms belonging to two different atomic lines from the same pair. c) Height profiles covering two lines along a) XX' (filled electronic states) and b) YY' (empty states). Notice that as for isolated atomic lines, the Si-Si dimer is symmetric.

Since these Si atomic lines have their length limited by the substrate only, i.e. by the steps, it is challenging to explore if one can built extremely long atomic lines on very large terraces. Most interestingly, Fig. 6 shows spectacular self-assembled Si atomic lines on such very large terraces. One can see that they are forming a network of massively parallel atomic lines having a length reaching micron scale (several thousands atoms), and probably much longer [33]. Despite such very long lengths, these Si atomic lines still remain very straight. This achievement results in probably what are the longest atomic lines ever built on a surface [33].

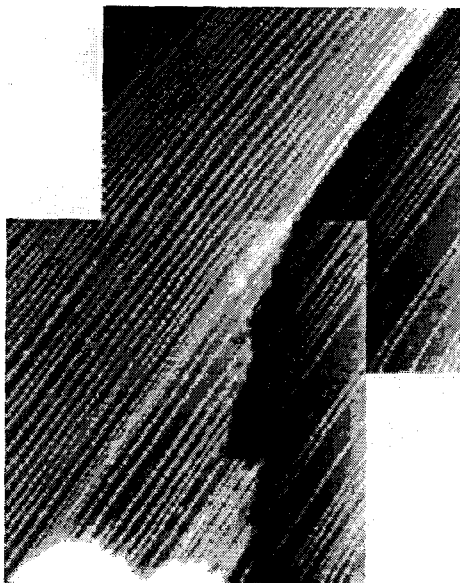


Figure 6. Imaging very long Si atomic lines on a large β -SiC(100) surface: two assembled 2000 Å x 2000 Å filled electronic state STM topographs. This gives atomic lines having lengths over 0.4 μm and much longer since the data acquisition was limited by the scanning capabilities of the AFM/STM instrument used here. These atomic lines, which form a network of "massively parallel" chains, are probably the longest one's ever built on a surface.

4 High temperature dynamics and dismantling of Si atomic lines

In order to explore the stability of these atomic lines, to study their dynamics and to reach the threshold of their dismantling, high temperature STM experiments are performed [38]. Fig. 7 exhibits series of STM topographs (filled electronic states) recorded at surface temperatures ranging from 25 °C to 900 °C [38]. These Si atomic lines are stable at 600 °C and 700 °C with none of them broken at such high temperatures [38]. At 700 °C, they are regularly spaced while the situation seems to change at 800 °C: although almost all dimer lines are still not broken, one can see

some gradual changes with very few vacancy segments and an apparent higher line density at the step edge. The latter feature indicates that atomic lines are moving one by one perpendicularly to the line direction and probably eliminated a collective mechanism at the step edge.

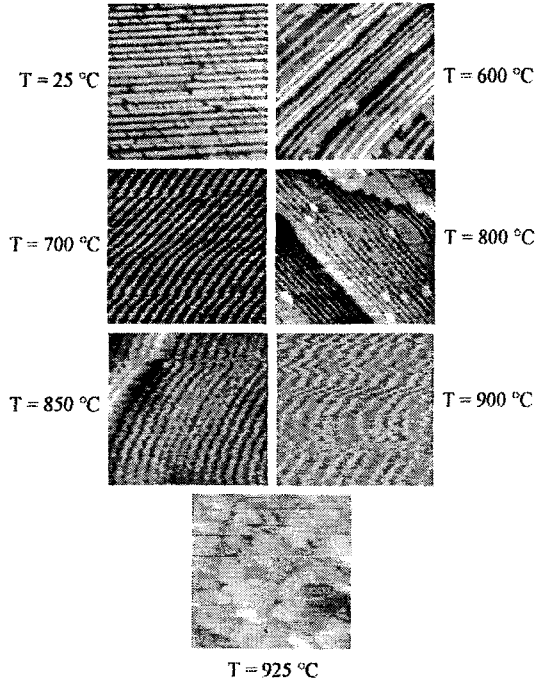


Figure 7. 300 Å x 300 Å STM topographs of Si atomic dimer lines on the β -SiC(100) surface imaged at temperatures ranging from 25 °C to 925 °C. Note that some of these topographs have been recorded on different surfaces and that the difference in Si line density does not necessarily result only from the effect of the temperature. At 800 °C, one can already notice the variations in line density in particular at the step edge.

When the temperature is raised to 850 °C and 900 °C, one can observe that the atomic lines are "sizzling" probably due to the large stress resulting from increasing temperatures, but it is also possible that such high temperatures might correspond to the STM instrumental limitation. Anyway, one can clearly notice that the atomic Si lines are still not broken. When the surface temperature is raised by 25 °C at 925 °C, one can see that the threshold of temperature-induced atomic line dismantling has been reached with only few lines remaining and Si island formation taking place [38]. This means that at 925 °C, the Si atom back bonds are broken leading to Si surface migration with island formation. This further shows that the bonding of the Si dimers with the silicon carbide substrate is very strong which, together with a strong dimer-dimer interaction along the atomic line are at the origin of their unprecedented stability. Incidentally, these STM experiments represent the

highest temperature atom resolved imaging. Subsequently and as far as we know, they also show what is probably the highest temperature stability ever achieved for nanostructures built on a surface [38].

Let us now look at the temperature-induced dynamics. Fig. 8 displays a serie of STM topographs (filled electronic states) for the same area of Si atomic lines that

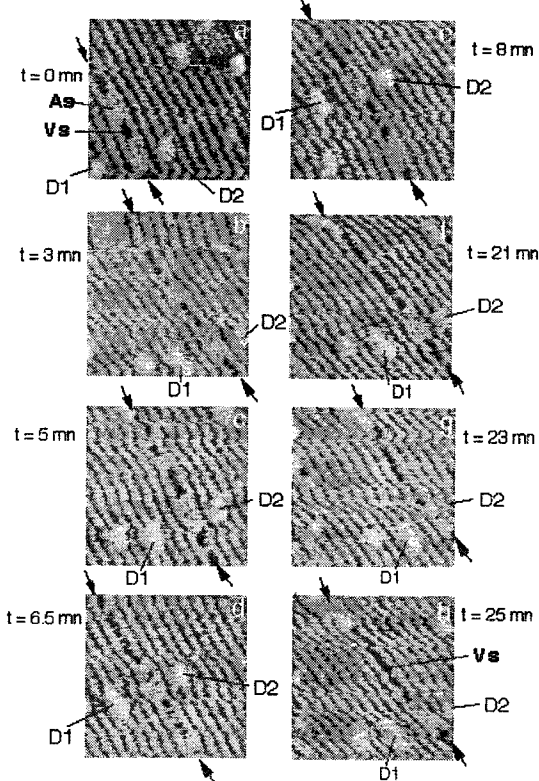


Figure 8. Dynamics of Si dimer lines at 800 °C shown on a serie of 100 Å x 100 Å STM topographs. We follow the dismantling with time (between 0 and 25 min) of the Si atomic line labeled *XX'* into atomic segments (As) and vacancy segments (Vs) (a to h). Two defects labeled D1 and D2 are used as landmarks to follow the evolution of the same measurement area.

are recorded during 25 min at 800 °C [38]. We follow with time the behavior of an atomic segment line (AS) and a vacancy segment (VS) indicated by an arrow in Fig. 8 which displays such a sequence. We have 8 representative STM topographs (a to h) of the same 100 Å x 100 Å area, all recorded at 800 °C. As landmarks to follow the evolution of the same measurement, two defects D1 and D2 are used and keep the same position with the atomic line density remaining about the same except for one, labeled *XX'* which is of particular interest. The latter, located between D1 and D2, appears to be discontinued with two atomic segments labeled

As 1 (9 dimers) and As 2 (8 dimers) separated by a vacancy segment Vs (about 5 missing dimers), the distance between two dimers along a Si line being 6.16 Å [16, 19]. As 1, As 2 and Vs evolution with time is followed at a 800 °C constant temperature. In Fig. 8(b), one can see that, after 3 min, As 1 and As 2 exhibit the loss of one and two dimers respectively with Vs becoming longer (7 missing dimers) indicating that As 2 is also moving away from As 1 which remains stable. Two minutes later (Fig. 8(c)), As 1 shows no change while As 2 has lost additional dimers resulting in an increased vacancy segment VS length by one dimer. At 7 min, As 2 has only one dimer left with Vs reaching a length corresponding to about 14 missing dimers. This suggests that the remaining As 2 is still moving away from As 1 (Fig. 8(d)). From 8 to 25 min, the last dimer belonging to As 2 has disappeared, leading to the opening of a much longer vacancy segment Vs (> 25 missing dimers). This sequence shows that the Si atomic line dismantling also results from an individual mechanism with one-by-one dimer removal [38].

Also we have found that at temperatures above 800 °C, the Si atomic lines are also moving laterally with a higher line density at the step edges. This suggests that the lines are removed one-by-one at the step edges. So the Si thermal elimination on the β -SiC(100) surface results from both individual (one-by-one dimer removal) and collective (line-by-line removal at the step edges) mechanisms [38]. These interesting features are also experimentally advantageous since they probably limit the Si evaporation onto the STM tip, therefore making atomic scale STM imaging at such extreme temperatures somewhat easier. Overall, these experiments stress once again the strong interaction between Si dimers belonging to the same line, this interaction possibly taking place through the SiC surface.

5 New developments and perspectives

We have shown that it is possible, to control at the atomic scale, surfaces and nanostructures on silicon carbide. The Si atomic lines that are self-organized on the SiC surface have unprecedented characteristics since they probably have the highest thermal stability (900 °C) + the longest lengths (μm range) ever observed for an atomic line built on a surface. It is also possible to monitor the line density/spacing in a single step process, thermal annealing, with arrangements ranging from a single isolated Si atomic line to a large super-lattice of massively parallel atomic lines. If one compares with a line network of an integrated circuit from the late 80's/early 90's (Fig. 9), one can notice that the line density that can be achieved with the Si atomic lines are several orders of magnitude larger. All things being equal, the surface covered by Si atomic lines are 10^{+8} smaller than those covered by Cu or Al lines.

We have also recently found that, by selective adsorbate deposition, the reactivity of these lines with molecules or metal atoms could be very different from that of the underlying surface. This feature open-up many possibilities to built

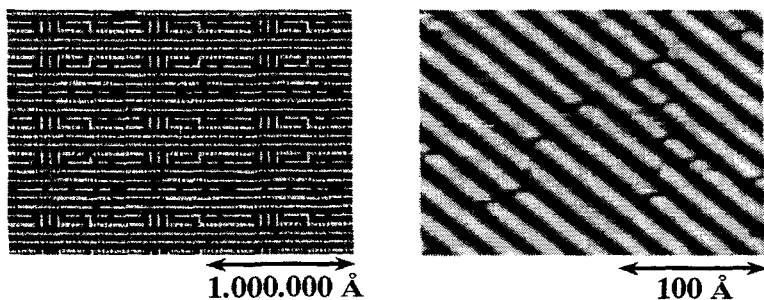


Figure 9. Size comparison between a late 80's/early 90's integrated circuit ($40\ \mu\text{m} \times 28\ \mu\text{m}$) and a super lattice ($250\ \text{\AA} \times 175\ \text{\AA}$) of Si atomic lines. The latter has a surface nearly 8 orders of magnitude smaller.

nanostructures having very versatile properties. Applications are therefore possible in nanoelectronics, the nanometer scale being recently reached for devices such as a 1.5 nm transistor as already successfully achieved at IBM [42], but also in catalysis or in nanochemistry, since such Si atomic lines could be used as a template e.g. in polymer fabrication by assembling several monomers. The characteristics of these Si atomic lines not only meet but in some cases exceed the requirements for nanotechnology as described in the National Nanotechnology Initiative White House Report [41]. These systems represent model cases in nanophysics.

6 Acknowledgments

The author is especially grateful to his PhD and former PhD students in particular to Fabrice Semond, Vincent Derycke and Fabrice Amy, to his collaborators Victor Aristov, Ludovic Douillard and Hanna Enriquez, and to his graduate students Pascal Fonteneau, Nga-phuong Pham and Pierrick Condette. He also want to thank Andrew Mayne, Gérald Dujardin and the Laboratoire de Photophysique Moléculaire in Orsay where part of the room temperature STM measurements have been performed. Very high quality SiC samples have been provided by Thierry Billon, Lea di Ciccio and their group at CEA-LETI (Grenoble), by Yves Monteil and his group at LMI-Université Claude Bernard (Lyon) and by André Leycuras at CRHEA-CNRS (Sophia Antipolis).

References

1. Moisan H., *Comptes Rendus de l'Académie des Sciences* (Paris) **139** (1904) 773.
2. *Silicon Carbide*, ed. by Choyke W. J., Matsunami H .M., Pensl G., (Akademie Verlag, Berlin, 1998); references therein.

3. Capano. M. A., Trew R. J., Silicon Carbide Electronic Devices and Materials, *MRS Bulletin* **22** (1997) 19-22 , references therein.
4. Silicon Carbide Electronic Devices, *IEEE Trans. Electron Dev.* **46** (1999); references therein.
5. Keyes R. W., *Proc. IEEE* **60** (1972) 225.
6. Johnson E. O., *RCA Rev.* **26** (1965) 163.
7. Diamond Detector Devices and Materials, *MRS Bulletin*, **23** (1998).
8. Soukiassian P., Semond F. *J. Physique IV (France)* **7** (1997) 10; references therein.
9. Soukiassian P., Dujardin G., *La Recherche* **321** (1999) 38; references therein.
10. Aroutiounian V. M., Bouniatian V.V., Soukiassian P., *Sol. Stat. Electronics* **43** (1999) 343; *IEEE Trans. Electron Dev.* **46** (1999) 585.
11. Starke U., Schardt J., Berhardt J., Franke M., Heinz K., *Phys. Rev. Lett.* **82** (1999) 2107.
12. Bermudez V. M., *Phys. Stat. Sol. (b)* **202** (1997) 447, references therein.
13. Soukiassian P., *Mat. Sci. Eng. B* **61** (1999) 506, references therein.
14. Semond F., Soukiassian P., Mayne A., Dujardin G., Douillard L., Jaussaud C., *Phys. Rev. Lett.* **77** (1996) 2013.
15. Soukiassian P., Semond F., Douillard L., Mayne A., Dujardin G., Pizzagalli L., Joachim C., *Phys. Rev. Lett.* **78** (1997) 907.
16. Soukiassian P., Semond F., Mayne A., Dujardin G., *Phys. Rev. Lett.* **79** (1997) 2498.
17. Powers J. M., Wander A., Rous P. J., Van M. A.Hove, Somorjai G. A., *Phys. Rev. B* **44** (1991) 11159.
18. Long J. P., Bermudez V. M., Ramaker D. E, *Phys. Rev. Lett.* **76** (1996) 991.
19. Semond F., *Ph. D. Thesis*, Université de Paris-Sud/Orsay, 1996.
20. Derycke V., Soukiassian P., Mayne A., Dujardin G., Gautier J., *Phys. Rev. Lett.* **81** (1998) 5868.
21. Derycke V., Soukiassian P., Mayne A., Dujardin G., *Surf. Sci. Lett.* **446** (2000) L101.
22. Soukiassian P., Aristov V. Yu., Douillard L., Semond F., Mayne A., Dujardin G., Pizzagalli L., Joachim C., Delley B., Wimmer E., *Phys. Rev. Lett.* **82** (1999) 3721.
23. Douillard L., Aristov V.Yu., Semond F., Soukiassian P., *Surf. Sci. Lett.* **401** (1998) L395.
24. Yeom H. W., Shimomura M., Kitamura J., Hara S., Tono K., Matsuda I., Mun B. S., Huff W. A. R., Kono S., Ohta T., Yoshida S., Okuski H., Kajimura K., Fadley C. S., *Phys. Rev. Lett.* **83** (1999) 1640.
25. Aristov V. Yu., Douillard L., Fauchoux O., Soukiassian P., *Phys. Rev. Lett.* **79** (1997) 3700.
26. Yan H., Smith A. P., Jónsson H., *Surf. Sci.* **330** (1995) 265.
27. Sabisch M., Krüger P., Mazur A., Rohlfing M., Pollmann J., *Phys. Rev. B* **53** (1996) 13121.

28. Käckell P., Furthmüller J., Bechtold F., Kresse G., Hafner J., *Phys. Rev. B* **54** (1996) 10304.
29. Catellani A., Galli G., Gygi F., *Phys. Rev. Lett.* **77** (1996) 5090.
30. Catellani A., Galli G., Gygi F., Pellacini F., *Phys. Rev. B* **57** 12255 (1998).
31. Douillard L., Sernoud F., Aristov V. Yu., Soukiassian P., Delley B., Mayne A., G. Dujardin, E. Wimmer, *Materials Science Forum* **264** (1998) 379.
32. Lu W., Krüger P., Pollmann J., *Phys. Rev. Lett.* **81** (1998) 2292.
33. Derycke V., *Ph. D. Thesis*, Université de Paris-Sud/Orsay, 2000.
34. Enriquez H., Derycke V., Aristov V. Yu., Soukiassian P., Le Lay G., Cricenti A., Croti C., Ferrari L., Perfetti P., *Appl. Surf. Sci.* **162** (2000) 559.
35. Derycke V., Fonteneau P., Soukiassian P., *Phys. Rev. B* **62** (2000) 12660.
36. Aristov V. Yu., Enriquez H., Derycke V., Soukiassian P., Le Lay G., Grupp C., Taleb-Ibrahimi A., *Phys. Rev. B* **60** (1999) 16553.
37. Derycke V., Nga Phuong Pham, Fonteneau P., Soukiassian P., Aboulet-Nze P., Monteil Y., Mayne A. J., Dujardin G., Gautier J., *Appl. Surf. Sci.* **162** (2000) 413.
38. Aristov V. Yu., Douillard L., Soukiassian P., *Surf. Sci. Lett.* **440** (1999) L285.
39. Whitman L. J., Stroscio J. A., Dragoset R. A., Celotta R. J., *Science* **251** (1991) 1206.
40. Shen T. C., Wang C., Abaln G. C., Tacker J. R., Lyding J. W., Avouris Ph., Walkup R. E., *Science* **268** (1995) 1590.
41. Nanotechnology Research Directions: Vision for Nanotechnology R&D in the Next Decade. National Science and Technology Council, The White House, 1999.
42. Martel R., Schmidt T., Shea H. R., Hertel T., Avouris P., *Appl. Phys. Lett.* **73** (1998) 2447; R. Martel, H.R. Shea, P. Avouris, *Nature* **398** (1999) 299.

INVITED

FORMATION OF SILICON AND GERMANIUM NANOSTRUCTURES USING ULTRATHIN SiO₂ FILMS

M. ICHIKAWA

*Joint Research Center for Atom Technology
1-1-4 Higashi, Tsukuba, Ibaraki 305-0046, Japan*

E-mail: ichikawa@jrkat.or.jp

Using a scanning reflection electron microscopy (SREM) and a high-temperature scanning tunneling microscopy (STM), we study formation processes of Si and Ge nanostructures on Si substrates covered with ultrathin SiO₂ films. It is found that windows are formed in the SiO₂ films by focused electron beams used for SREM or field emission (FE) electron beams from STM tips during heating of the samples. Ge nanoislands are formed by Ge deposition into the windows in the ultrathin SiO₂ films and subsequent annealing of the samples. The islands are formed only at the window positions. Si or Ge nanocrystals are also formed in the windows produced with the FE electron beams by selective growth using Si₂H₆ or GeH₄ gases. It is further found that Ge nanoislands with about 7 nm size and ultrahigh density ($>10^{12}$ cm⁻²) are grown on the ultrathin SiO₂ films. These nanoislands can be manipulated by STM when they are separated from Si substrates by the ultrathin SiO₂ films. These results imply new methods for forming Si and Ge quantum structures at given areas.

1 Introduction

The growth processes on Si proceed through the Stranski-Krastanov (SK) growth mode in which two-dimensional (2D) wetting layers with specific surface structures are formed up to about several atomic layers of Ge. Three dimensional (3D) islands then appear in the thicker areas of the Ge layers [1,2]. The self-assembling technique based on the SK growth mode has received a lot of attention in the fabrication of nanometer-scale islands. Formation of the islands using the SK growth mode has been successfully demonstrated for highly strained heteroepitaxial systems such as InGaAs on GaAs [3,4] and Ge on Si [5,6]. The self-assembling technique, however, should be improved to control the spatial arrangement of islands, reduce the island size and increase the island density. For this purpose, some attempts have been done to fabricate nanoislands with given spatial distributions on the surface by controlling surface morphologies of Si substrates [7,8]. In this study, we demonstrate that controlled 3D Si and Ge island formation at given areas can be carried out on Si surfaces by using ultrathin SiO₂ films.

2 Experimental methods

The experiments were performed using scanning reflection electron microscopy (SREM) with multi-functions [9] and high-temperature scanning tunneling microscopy (STM) [10]. In the SREM, an ultra-high vacuum scanning electron microscope (SEM) and STM are combined, enabling us to observe simultaneously the same areas with SEM or SREM and STM. SREM is a kind of SEM where a diffracted electron beam intensity in reflection high-energy electron diffraction (RHEED) pattern is used as an image signal to obtain SEM images. This combination also makes it possible to observe a STM tip apex after nanostructure fabrication with STM.

Clean Si surfaces were prepared by several flash direct-current heating to 1200 °C. To oxidize the surface, we raised the sample temperature from room temperature to 620 °C for 10 min after molecular oxygen had been introduced into the chamber at a pressure of 2×10^{-6} Torr. The thickness and chemical composition of the oxide films were characterized by producing oxide films under the same conditions in a separate X-ray photoelectron spectroscopy system [11]. The film thickness was estimated to be about 0.3 nm and the oxide films were mainly composed of SiO_2 .

A Knudsen cell with a PBN crucible was used to deposit Ge in the SREM chamber and chemical beams of Si_2H_6 and GeH_4 gases were used to perform selective growth in the STM chamber.

3 Results and discussion

3.1 *Si window formation in ultrathin SiO_2 films on Si substrates*

We have developed a technique to form Si windows in ultrathin SiO_2 films on Si surfaces. The focused electron beam (EB) used for SREM was linearly scanned on an Si(111) wafer covered with ultrathin SiO_2 film at room temperature (RT) and it was heated at 750 °C for 30 s. Fig. 1 shows a SREM image of the sample. The contrast in the EB-irradiated areas hardly changed after EB irradiation at RT but the EB irradiated areas brightened after heating. The bright line area in Fig.1 showed microprobe RHEED pattern from the 7×7 structure. There was a 1×1 structure outside the bright line area. This indicates that clean Si substrate surface window appeared on the bright area as a result of selective thermal decomposition in the SiO_2 film induced by EB irradiation. Si windows with 10 nm scale were produced in the SiO_2 film. The minimum size of the window was 7 nm [12].

The mechanism of the selective thermal decomposition of SiO_2 was studied by scanning Auger microscopy [11]. It is well known that oxygen is desorbed from SiO_2 films due to the Auger process initiated by EBs. We found that SiO_2 films

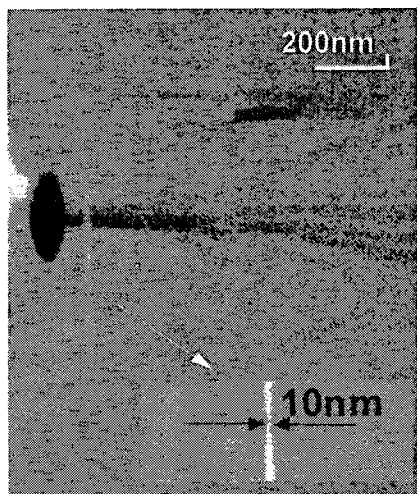


Figure 1. SREM image of ultrathin SiO_2 -covered Si(111) surface after EB irradiation at RT and subsequent annealing.

changed to SiO -like films due to the oxygen desorption [13]. When the sample was heated, the SiO -like films changed to volatile SiO gas, resulting in selective thermal decomposition from the EB-irradiated areas. The effect of secondary electrons is small in this process, since core level excitation energy larger than 30 eV is needed for EB-stimulated oxygen desorption [14]. This indicates that the window size is mainly determined by the EB diameter.

We have also developed a technique to form windows in ultrathin SiO_2 films on Si surfaces by using field emission (FE) electron beams from STM tips [15]. Oxidized Si samples were heated to 450–630 °C. The sample surfaces were then irradiated with electron beams from a STM tip having an energy of 70–150 eV and a current of 10–50 nA. During electron beam irradiation, the STM tip was held at 70–250 nm from the sample surface to avoid destruction caused by high electric field between the surface and the STM tip. Then, the STM tip was approached to the surface and STM observations were done at a tunneling current of 60 pA and a sample bias of 4 V to obtain stable oxide surface images.

Fig. 2(a) shows a typical STM image of the oxidized Si(111) surface at a substrate temperature of 630 °C. Zigzag lines correspond to atomic steps. Fig. 2(b) shows a STM image of the oxidized surface after FE electron beam irradiation with the electron energy of 70 eV. The electron beam irradiated area is round with diameter of about 40 nm. To see the morphology of the electron beam irradiated area more clearly, an enlarged STM image is shown in Fig. 2(c). The 7×7 atomic structure can be seen, indicating that the clean Si(111) -7×7 surface appeared in the window area.

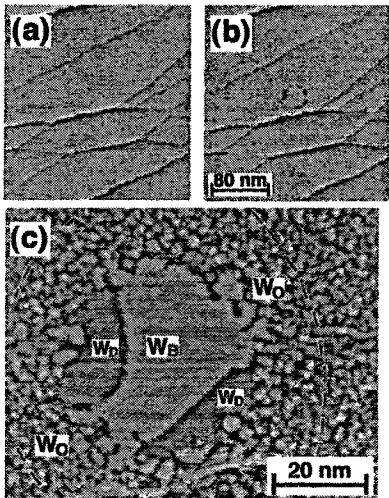


Figure 2. STM images of an oxidized Si(111) surface at 630 °C (a) before and (b) after fabrication. (c) Enlarged STM image of the fabricated area. W_B and W_D show Si window and W_O shows partially EB irradiated area.

3.2 *Ge nanoisland formation at given areas on Si(111)*

Point-shaped Si window array (6x6) was formed on an ultrathin SiO_2 -covered Si(111) surface by irradiating focused electron beams used for SREM [16]. Then 2.6 bilayer (BL) thick Ge layers were deposited on the oxidized Si(111) surface at 550 °C. Epitaxial and some Ge films grew on the windows and SiO_2 areas, respectively as shown in a SREM image of Fig. 3(a). The detailed property of the

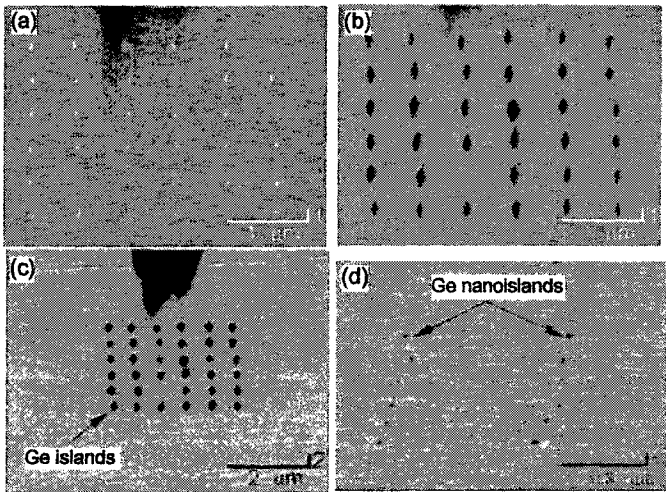


Figure 3. SREM images showing Ge nanoisland growth processes using ultrathin SiO_2 films.

Ge films on the oxide surface will be described in the next section. When the sample was annealed at 690 °C for 5 min, the SiO₂ film reacted with the deposited Ge films, and Ge islands grew in the window areas as shown in Fig. 3(b). It is noted that the Ge islands were grown in the window areas without any Ge islands outside the window areas.

During annealing of the sample, the SiO₂ film was decomposed as a result of the following reaction: $\text{Ge} + \text{SiO}_2 \rightarrow \text{SiO}(\text{gas}) + \text{GeO}(\text{gas})$. At the same time, excess Ge diffused to the window areas. The effective thickness became larger than 3 BLs in the window areas and Ge island nucleation started due to Stranski-Krastanov growth. The island size became larger during annealing by further Ge diffusion to Ge islands from the unstable two-dimensional (2-D) layer, as shown in Fig. 3(c). At this growth condition, the Ge island size is about 200 nm. However, we can fabricate much smaller Ge islands when the Ge thickness was decreased. Fig. 3(d) shows a SREM image of the same treated sample after deposition of 2 BL Ge at 550 °C and subsequent annealing at 690 °C for 10 min. Ge nanoislands 10 nm in size grew only in the window areas due to the decrease of the nominal Ge layer thickness.

3.3 Ge nanoisland formation with ultra-high density on ultrathin SiO₂ films

We have recently found that Ge nanoislands with 7 nm in size and ultrahigh density grew on the ultrathin SiO₂ film surfaces [17]. Figs. 4(a) and (b) show a STM image and a microprobe RHEED pattern after 2.0 BL Ge deposition on an ultrathin SiO₂-covered Si(111) surface at 390 °C. Hemispherical Ge nanoislands with 7 nm in average size and ultrahigh density of about $2 \times 10^{12} \text{ cm}^{-2}$ were grown on the surface.

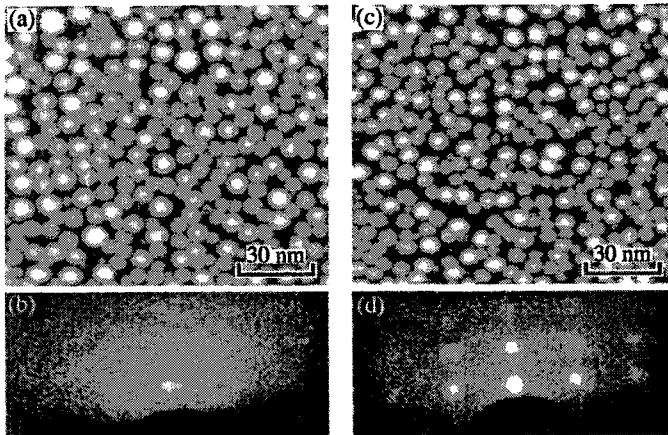


Figure 4. STM images and RHEED patterns after 2 BL Ge deposition at 390 °C ((a) and (b)) and at 450 °C ((c) and (d)).

The microprobe RHEED pattern shown in Fig. 4(b) shows Debye-Scherrer ring pattern, indicating that non-epitaxial Ge nanoislands to the Si substrate grew on the SiO₂ surface. Fig. 4(c) and (d) show a STM image and microprobe RHEED pattern after 2.0 BL Ge deposition on the surface at higher temperature of 450 °C. The microprobe RHEED pattern shows a spotty pattern, indicating that the Ge nanoislands grew having the epitaxial relation with the Si substrate.

In spite of the fact that Ge was deposited on the amorphous SiO₂ films, the RHEED pattern (Fig. 4(d)) shows that Ge nanoislands were epitaxially grown on the Si(111) substrate at higher temperatures. The Ge deposition can create areas of bare Si through the reaction: $\text{Ge} + \text{SiO}_2 \rightarrow \text{SiO}(\text{gas}) + \text{GeO}(\text{gas})$, in which the evaporation of SiO and GeO is enhanced at higher temperatures. These Si bare areas provided conditions for the epitaxial growth of Ge nanoislands. At lower temperatures shown in Figs. 4(a) and (b), bare Si areas were not created, resulting in the growth of non-epitaxial Ge nanoislands. It was found that the island density hardly depended on the deposition rate, indicating that it was mainly determined by Ge chemical reactions with the ultrathin SiO₂ films.

We have also found that the non-epitaxial Ge nanoislands can be manipulated by STM [18]. Figs. 5(a) and (b) show STM and height profile along the line between arrows after the STM tip scanned for 3 min in area 60x60 nm² at the tip bias voltage of -4.0 V under EB irradiation used for SREM. The Ge nanoislands could be removed from the scanned area. The removal process was also performed on the bare SiO₂ surface in the middle of the area for about two times longer than that for the Ge removal. A pit of about 2-nm deep appeared, indicating that ultrathin SiO₂ was completely removed and Si bare surface appeared at this area. The experimental results suggest that the EBs initiate fluctuations of the tunneling current and vibrations of the tip. Under these conditions, removal of non-epitaxial Ge nanoislands takes place through chemically-assisted field evaporation in which the tip almost contacts with the Ge islands.

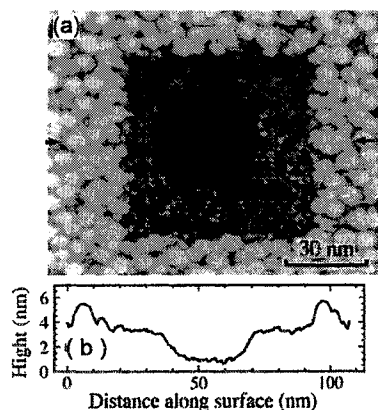


Figure 5. (a) STM image of Ge nanoislands on ultrathin SiO₂ film after fabrication. (b) Height profile along the line between arrows in (a).

3.4 Selective growth and stability of Si nanocrystal in windows

Si nanocrystals were formed using selective epitaxial growth on Si in the windows in ultrathin SiO_2 as shown in Fig. 6. Fig. 6(a) shows a STM image of the ultrathin SiO_2 -covered $\text{Si}(001)$ surface after fabrication at 550°C . The FE electron beam irradiation (90 eV) was performed when the STM tip was 130 nm from the sample surface. A clean $\text{Si}(001)$ - 2×1 surface window appeared at the FE electron irradiated area. Fig. 6(b) shows a STM image after 7 min growth at 550°C using Si_2H_6 gas. A pyramidal nanocrystal with $\{111\}$ facets on the side walls grew in the window. At this growth condition, layer-by-layer Si film growth takes place on clean flat $\text{Si}(001)$ - 2×1 surfaces. This indicates that the growth of pyramidal Si nanocrystal is specific one when the growth area is confined in nanometer scale areas. We found that the pyramidal structure was formed due to repulsive interaction between double layer steps (D_B steps to which the Si dimer rows are perpendicular) which compose $\{111\}$ facets [19].

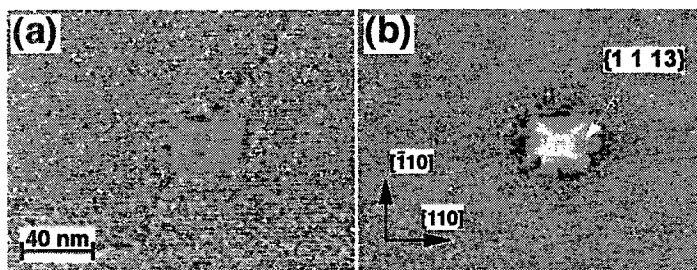


Figure 6. STM image of Si selective growth on the $\text{Si}(001)$ in the window at 550°C . (a) After fabrication. (b) 7 min after Si growth started.

We also found that the pyramidal Si nanocrystals are stable at high temperature when they are surrounded by the SiO_2 films. Fig. 7(a) shows a STM image of a Si nanocrystal grown on a Si window after Si_2H_6 supply at 600°C . Fig. 7(b) shows the image of the sample in (a) after 34 min annealing at 600°C .

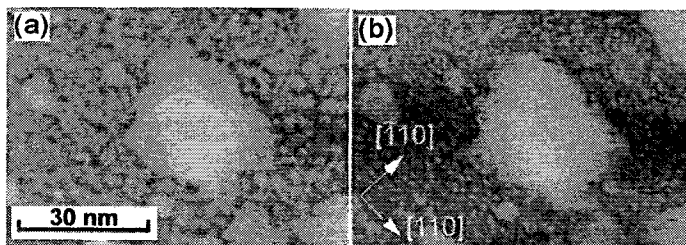


Figure 7. STM images showing the stability of Si nanocrystals at high temperature. (a) Si nanocrystal grown on $\text{Si}(001)$ in the window after Si_2H_6 supply at 600°C . (b) The nanocrystal after 34 min annealing at 600°C .

The pyramidal shape of the Si nanocrystal was preserved after annealing. This indicates that Si nanocrystals are stable in the window at high temperature with the initial pyramidal structure. The stability is caused by the fact that the potential energy barrier (larger than 3 eV) at the window boundary reflects Si adatoms detached from the steps of the crystal and confine the adatoms within the window area. The potential barrier originates from the difference in the adsorption energy of Si adatoms on SiO₂ surfaces (~1 eV) and those on Si(001) surfaces (~5 eV). This property is generic one that is expected for some passivated Si surfaces such as hydrogen-, nitrogen- and metal-passivated Si surfaces.

3.5 Selective growth of Ge, Ge/Si and Si/Ge/Si nanoislands on Si in windows

We formed Ge nanoislands using selective epitaxial growth in windows using GeH₄ gas [20]. Fig. 8 shows STM images before and after the growth had started. By FE electron beam irradiation, a window with a diameter of about 40 nm was formed (Fig. 8(a)). Initially, 2D growth proceeded along the [110] directions and a patch-like pattern was formed (Fig. 8(b)). The thickness of several points in the window reached more than 3 monolayers (ML). These points are thought to be nucleation sites of 3D Ge islands. The shape of these islands was irregular in the initial stage of the 3D growth but gradually changed to {105} facets parallel to the [010] directions (Fig. 8(c)). As the islands grew, the {105} facets became larger and clearer. Several islands coalesced and finally only one hut-like island was formed in the window (Fig. 8(d)).

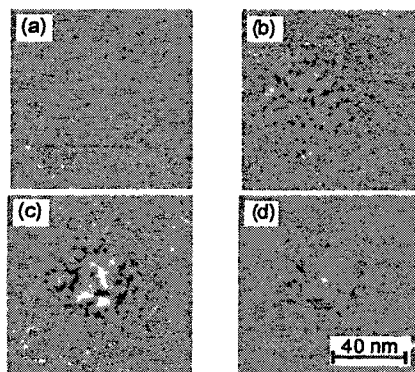


Figure 8. STM images of Ge selective growth Si(001) in the window formed by STM tip. (a) After window formation, (b) 75 min, (c) 3 h and (d) 6.5 h after GeH₄ supply at 410 °C.

Fig. 9(a) shows ultrathin SiO₂-covered Si(001) surface in which 25 windows were formed by FE electron beams at 410 °C. Fig. 9(b) shows the sample surface after GeH₄ supply at 410 °C. Ge nanoislands 20 nm in size were selectively grown

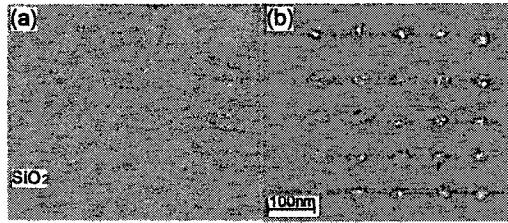


Figure 9. STM images of a Si(001) surface: (a) after window formation using STM tip, (b) after Ge selective growth.

in the window areas. The Ge nanocrystals were also stable at high temperature when they were surrounded by the SiO_2 film. Such stable Si nanocrystals or Ge nanocrystals have a useful property to form Si-based hetero-nanostructures at elevated temperatures.

We formed Si/Ge/Si hetero-nanoislands with specific facet structures in the window areas. Fig. 10 shows STM images of Ge selective overgrowth at 410°C on a Si nanocrystal with $\{119\}$ facets on the side walls (Fig. 10(a)). $\{105\}$ facets appeared at the corners of the islands, which grew faster than the $[110]$ -related facets on the side walls (Fig. 10(b)). Finally the island became hut-like shape with $\{105\}$ facets (Fig. 10(c)). Furthermore, Si_2H_6 gas was supplied on these Ge/Si nanoislands to form three-dimensionally embedded Ge structures. The shape of the nanoislands changed to that having mainly $\{113\}$ facet structures. Photoluminescence spectra from these islands showed a broad peak with the central position of 0.9 eV , which was originated from the embedded Ge nanoislands.

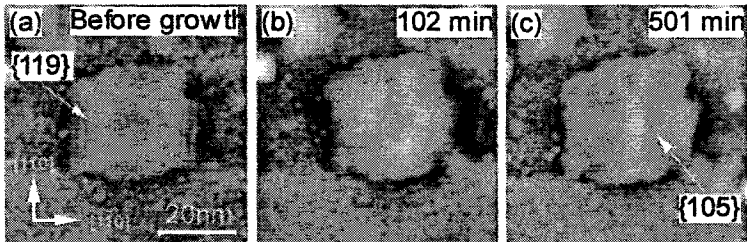


Figure 10. STM images during GeH_4 supply on a Si nanocrystal with $\{119\}$ facets at 410°C .

4 Summary

Using a scanning reflection electron microscopy and a high-temperature scanning tunneling microscopy, we studied formation processes of Si and Ge nanostructures on Si substrates covered with ultrathin SiO_2 films. Windows were formed in the

SiO₂ films by focused electron beams used for SREM or field emission electron beams from STM tips during heating samples. Ge nanoislands were formed by deposition of Ge on Si in the windows in ultrathin SiO₂ films and subsequent annealing of the samples. The islands were formed only at the window positions. Si or Ge nanocrystals were also formed in the Si windows produced with the FE electron beams by selective growth using Si₂H₆ or GeH₄ gases. It was further found that Ge nanoislands of about 7 nm in size and ultrahigh density ($>10^{12}$ cm⁻²) were grown on the ultrathin SiO₂ films. These nanoislands could be manipulated by STM when they were separated from Si substrate by ultrathin SiO₂ films. These results imply new methods for the formation of Si and Ge quantum structures at given areas.

5 Acknowledgements

This work was done in collaboration with Ichikawa group members. This was supported by the New Energy and Industrial Technology Development Organization (NEDO), and the National Institute for Advanced Interdisciplinary Research.

References

1. Köhler U., Jusko O., Pietsch G., Müller B., Henzler M., Strained-layer growth and islanding of germanium on Si(111)-(7x7) studied with STM, *Surf. Sci.* **248** (1991) pp. 321-331.
2. Motta N., Sgarlata A., Calarco R., Nguyen Q., Castro Cal J., Patella F., Balzarotti A., De Crescenzi M., Growth of Ge-Si(111) epitaxial layers: intermixing, strain relaxation and island formation, *Surf. Sci.* **406** (1998) pp. 254-263.
3. Leonard D., Krishnamurthy M., Reaves C. M., Denbaars S. P., Petroff P. M., Direct formation of quantum-sized dots from uniform coherent islands of InGaAs on GaAs surfaces, *Appl. Phys. Lett.* **63** (1993) pp. 3203-3205.
4. Xie Q., Madhukar A., Chen P., Kobayashi N. P., Vertically self-organized InAs quantum box islands on GaAs(001), *Phys. Rev. Lett.* **75** (1995) pp. 2542-2545.
5. Tersoff J., Teichert C., Lagally M. G., Self-organization in growth of quantum dot superlattices, *Phys. Rev. Lett.* **76** (1996) pp. 1675-1678.
6. Liu F., Lagally M. G., Self-organized nanoscale structures in Si/Ge films, *Surf. Sci.* **386** (1997) pp. 169-181.
7. Zhu J-H., Brunner K., Abstreiter G., Two-dimensional ordering of self-assembled Ge islands on vicinal Si(001) surfaces with regular ripples, *Appl. Phys. Lett.* **73** (1998) pp. 620-622.
8. Kamins T., Williams R., Lithographic positioning of self-assembled Ge islands on Si(001), *Appl. Phys. Lett.* **71** (1997) pp. 1201-1203.

9. Ichikawa M., Maruno S., Fujita S., Watanabe H., Kusumi Y., Microprobe RHEED/STM combined microscopy, *Surf. Rev. Lett.* **4** (1997) pp. 535-542.
10. Fujita K., Kusumi Y., Ichikawa M., Nucleation along step edges during Si epitaxial growth on the Si(111) surface observed by STM, *Surf. Sci.* **380** (1997) pp. 66-74.
11. Watanabe H., Ichikawa M., Development of a multifunctional surface analysis system based on a nanometer scale scanning electron beam, *Rev. Sci. Instrum.* **67** (1996) pp. 4185-4190.
12. Fujita S., Maruno S., Watanabe H., Ichikawa M., Nanofabrication using selective thermal desorption of SiO₂/Si induced by electron beams, *J. Vac. Sci. Technol. A* **15** (1997) pp. 1493-1498.
13. Watanabe H., Fujita S., Maruno S., Fujita K., Ichikawa M., Electron-beam-induced selective thermal decomposition of ultrathin SiO₂ layers used in nanofabrication, *Jpn. J. Appl. Phys.* **36** (1997) pp. 7777-7781.
14. Ueda K., Behaviors of hydrogen and oxygen on cleaned silicon surfaces, *Jpn. J. Appl. Phys.* **33** (1994) pp. 1524-1527.
15. Shibata M., Nitta Y., Fujita K., Ichikawa M., Nanometer-scale Si selective epitaxial growth on Si surface windows in ultrathin oxide films fabricated using scanning tunneling microscopy, *Appl. Phys. Lett.* **73** (1998) pp. 2179-2181.
16. Shklyayev A. A., Shibata M., Ichikawa M., Nanometer-scale germanium islands on Si(111) surface windows formed in an ultrathin silicon dioxide film, *Appl. Phys. Lett.* **72** (1998) pp. 320-322.
17. Shklyayev A. A., Shibata M., Ichikawa M., High-density ultrasmall epitaxial Ge islands on Si(111) surfaces with a SiO₂ coverage, *Phys. Rev. B* **62** (2000) pp. 1540-1543.
18. Shklyayev A. A. Ichikawa M., Electron-beam initiated transfer of Ge from Ge islands on SiO₂ surfaces to the tip of a scanning tunneling microscope, To be published in *Jpn. J. Appl. Phys.*
19. Shibata M., Nitta Y., Fujita K., Ichikawa M., Pyramidal Si nanocrystals with a quasiequilibrium shape selectively grown on Si(001) windows in ultrathin SiO₂ films, *Phys. Rev. B* **61** (2000) pp. 7499-7504.
20. Nitta Y., Shibata M., Fujita K., Ichikawa M., Nanometer-scale Ge selective growth on Si(001) using ultrathin SiO₂ film, *Surf. Sci.* **462** (2000) pp. L587-L593.

INVITED

HIGH TEMPERATURE SUPERCONDUCTING ARTIFICIAL SUPERLATTICES: TECHNOLOGY AND PERSPECTIVES

L. MARITATO

Unità di Ricerca INFN di Salerno

84081 Baronissi, Salerno, Italy

and

Dipartimento di Fisica, Università di Cagliari

Monerrato, Cagliari, Italy

E-mail: maritato@sa.infn.it

The realization and the study of artificially layered high temperature superconductivity systems is a field of growing interest for basic physics and practical applications. Here a non exhaustive review of some of the most interesting results in this area is given, with particular attention to three main classes of HTS artificial structures: $\text{YBa}_2\text{Cu}_3\text{O}_x$ based multilayers, $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ based layered systems and infinite layer based superlattices. A brief overview of the present applications and of the potential perspectives is also proposed.

1 Introduction

Soon after the discovery of high temperature superconductivity (HTS) in the layered cuprate oxides [1], its tight relation with the reduced dimensionality and the strong structural anisotropy present in such systems was immediately recognized and analyzed [2]. The confinement of transport properties in layers of few angstroms (the Cu-O_2 planes) experimentally observed in all the HTS cuprate oxides [2], clearly addressed the importance to study the role played by dimensional phenomena in these materials.

One of the experimental procedures to be used to analyze dimensional effects in HTS compounds is the realization of artificial superlattices in which superconducting layers are alternated with other kind of materials (normal metal, magnetic, semiconductor, superconductor). In this way it is possible to choose suitably not only the relative thicknesses of the system but also the type of coupling between successive superconducting layers. One important point to stress, in the case of HTS compounds, is that in this class of materials the superconducting behavior is very sensitive to local disorder [3], and that due to the very small values of the superconducting coherence lengths [2], even defects with size of the order of few angstroms, can be very deleterious of the superconducting properties. On the other hand, the growth of artificial superlattices in which different materials, with different lattice properties are superimposed, is a typical process in which disorder

is introduced in the system. The real time control of the structural properties down to an atomic level and the finding of materials with close lattice properties are therefore crucial in order to improve the epitaxial growth. From this point of view, the class of the perovskitic oxides to which all the HTS cuprates belong is extremely interesting, because many of these compounds show similar unit cell symmetries and in plane lattice parameters [4]. Moreover, in spite of these structural similarities, the cuprate oxide present a large variety of electronic behaviors going from insulating to metallic, from semiconducting to ferroelectric, from ferromagnetic to antiferromagnetic or spin glass [5]. This astonishing richness in their electronic properties is particularly interesting in view of the abundance of physical effects which can be studied in artificial superlattices and for the possible new applications that such layered systems can allow.

Several deposition techniques have been successfully used to produce epitaxial superlattices of HTS cuprate oxides. In particular, sputtering, molecular beam epitaxy (MBE) and pulsed laser ablation (PLA) have allowed to realize several kinds of HTS artificially layered systems showing atomically sharp interfaces with peculiar transport properties [5].

In the following we will focus on three HTS superlattice systems which have been extensively studied in the recent years: $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) based multilayers, $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ (BSCCO) based layered systems and infinite layer (IL such as BaCuO_2 or CaCuO_2) based superlattices. Finally, before drawing the conclusions, a short overview about recently proposed applications and possible perspectives in the use of HTS based layered systems in electronics will be given.

2 $\text{YBa}_2\text{Cu}_3\text{O}_x$ based multilayers

Following the work of Triscone et al. [6] who fabricated $\text{YBa}_2\text{Cu}_3\text{O}_x/\text{DyBa}_2\text{Cu}_3\text{O}_x$ multilayers using a sputtering technique, many research groups have analyzed transport properties of YBCO based superlattices in which the superconducting compound was intercalated with other cuprate oxides showing semiconducting or insulating behavior ($\text{DyBa}_2\text{Cu}_3\text{O}_x$, $\text{PrBa}_2\text{Cu}_3\text{O}_x$, $\text{PrBa}_2\text{Cu}_{3-x}\text{Ga}_x\text{O}_7$) [7]. The behavior of the critical temperature versus the relative thicknesses showed a dependence upon the interlayer coupling between successive superconducting layers [7,8]. Moreover, recent measurements in $\text{YBa}_2\text{Cu}_3\text{O}_x/\text{PrBa}_2\text{Cu}_3\text{O}_x$ multilayers where the thickness of $\text{YBa}_2\text{Cu}_3\text{O}_x$ was varied while that of the $\text{PrBa}_2\text{Cu}_3\text{O}_x$ layers was kept fixed [9], have indicated strong correlation between the intracell atomic structure and the critical temperature T_c . In particular, using an x-ray refinement technique, epitaxial mismatch strain was found to result in a surprising reorganization of interatomic distances in the unit cell which determined the decrease in T_c .

In Fig. 1 it is shown the dependence of several interatomic distances in the YBCO unit cell upon the YBCO thickness layer along with the T_c and c-axis behavior versus the same quantity. It is evident that T_c is in phase with the

changes of certain interatomic distances and with the c-axis value, while it is in antiphase with other intracell distances such as, for example, that between Ba atom and Cu-O₂ planes [9].

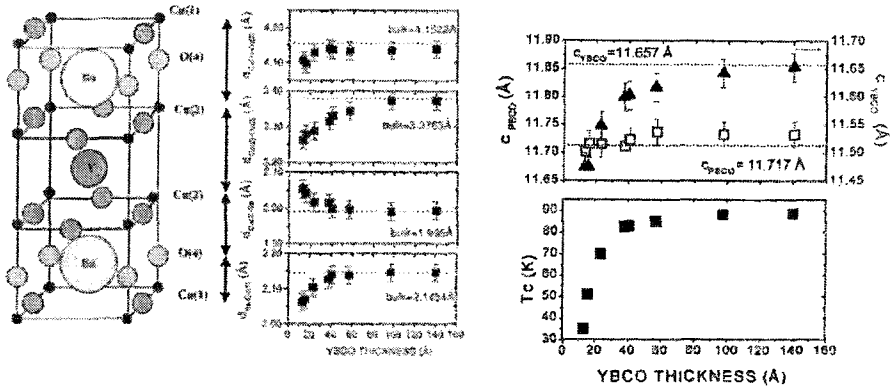


Figure 1. Changes in the main YBCO intracell distances along the c axis with the c axis value and the T_c behavior when changing YBCO layer thickness in YBa₂Cu₃O_x/PrBa₂Cu₃O_x multilayers [9].

Many other groups have fabricated YBCO based multilayers to analyze their vortex dynamic properties when varying the anisotropy of the system (i.e. the relative thicknesses). Generally, the pinning behavior depends on the coupling strength of YBCO layers [10], showing also dimensional cross over in agreement with the collective pinning theory [11]. Martinez et al. have recently reported about c-axis tunneling studies in YBa₂Cu₃O_x/PrBa₂Cu₃O_x multilayers using a suitable mesa geometry [12]. In the quasi two-dimensional limit (2 YBCO unit cells spaced with 7 PrBa₂Cu₃O_x unit cells), they found no clear superconducting coupling along the c axis but conductance spectra with a gap of about 5 meV. The spectra also showed quasi periodic structures attributed to the superlattice modulation. The authors suggested that this low value of the gap could be related to Cu-O chains in the YBCO structure [12].

3 Bi₂Sr₂Ca_{n-1}Cu_nO_x based layered systems

From the point of view of the structural coherence and the epitaxial growth of HTS superlattices the Bi₂Sr₂Ca_{n-1}Cu_nO_x family is an ideal candidate because of the similar values shown for the in plane lattice parameters allowing in principle perfect matching trough successive layers. In fact, the BSCCO compounds with n=1,2,3 have almost the same a and b parameter values of the orthorhombic unit cell, but different values of the c axis parameter, with different numbers of Cu-O₂ planes (respectively 1, 2, 3) per unit cell [4]. Moreover, transport properties of this family vary from insulating to metallic and to superconducting by slightly changing the

stoichiometric ratios at fixed n value. As an example, the compound with $n=1$, often indicated as 2201, can go from insulating to metallic and then to superconducting by changing the ratio between Sr and Bi atoms of only few percentages or by slightly varying the oxygen content [13].

Immediately after the discovery of this class of superconducting materials [1], layered artificial systems were grown using different deposition techniques. One of the first finding was that, contrarily to the case of YBCO based multilayers, BSCCO based superlattices showed almost unchanged superconducting properties even in the extreme bidimensional limit. For example, in sputtered, MBE and pulsed laser deposited $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x/\text{Bi}_2\text{Sr}_2\text{CuO}_x$ superlattices the critical temperatures were practically independent upon the thickness of the $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ layers and appreciably different from zero even when the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ layer was as thin as a single unit cell [14]. This was a strong indication of the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ bidimensional character as superconductor, in agreement with the higher anisotropy values shown by this compound when compared to those of YBCO.

At a first glance, the independence of T_c upon the layering in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x/\text{Bi}_2\text{Sr}_2\text{CuO}_x$ superlattices was interpreted as the demonstration that T_c was not influenced by the presence of the interfaces. Later works addressed such an influence and the possible enhancement in the critical temperature due to the presence of the compositional modulation [15]. In particular, in sputtered $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x/\text{Bi}_2\text{Sr}_2\text{CuO}_x$ superlattices an enhancement of T_c was observed to depend upon the electronic behavior of the $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ layers [16]. When these layers were insulating, their presence in the superlattice system reduced the critical temperature, while when the behavior of the 2201 layers was metallic, the 2212/2201 superlattices presented an enhanced T_c . This enhancement was observed only in systems with very thin layers of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$, while when the 2212 layers were thicker, T_c reduced to usual values.

The overall picture could be explained in terms of a charge transfer mechanism from 2201 to 2212 layers, obtaining an optimal carrier concentration in the last. It has been successively confirmed by other measurements on the same artificial system [15] and, as we will see in the next section, has opened the way to general interpretation of the superconducting behaviors observed in HTS cuprates. The development of fabrication techniques able to deposit atomic layer-by-layer artificial superlattices, has given the opportunity to obtain $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ phases with n higher than 3, which are not stable in bulk form. In particular, using an atomic layer-by-layer molecular beam epitaxy technique (ALLMBE), Eckstein, Bozovic et al. [17] have synthesized stable layers of the phase with $n=8$ inserting it in between 2201 layers, see Fig. 2. The high structural quality of the interfaces, down to atomic level, is clearly seen in the TEM image.



Figure 2. Cross sectional lattice image transmission electron micrograph of a metastable single $\text{Bi}_2\text{Sr}_2\text{Ca}_7\text{Cu}_8\text{O}_x$ layer inserted in a film of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ [17].

4 Infinite layer based superlattices

The charge transfer mechanism observed in BSCCO based layered structures, describes many of the behaviors seen in HTS cuprate oxides and especially their peculiar dependence of the critical temperature upon the charge carrier concentration in the Cu-O_2 planes [18]. Following this idea, one can model HTS compounds as the stacking of alternating blocks of atomic planes with different electronic properties, one, in which are present the Cu-O_2 planes, where the superconducting effects are confined, and the other behaving essentially as a charge reservoir. By looking at the structures of the HTS oxides, these blocks are generally made of infinite layer (IL) compounds (such as BaCuO_2 , CaCuO_2 or SrCuO_2) in direct contact between each other or separated by other atomic planes as, for example, Y planes or La planes [4]. One way to experimentally check this picture is the realization of new artificial superconducting layered systems obtained alternating different IL materials which, when taken by themselves are not even metallic. Moreover, the successful realization of such superlattices can also give the start to engineering of completely new superconducting materials, with suitably designed properties. In these artificial systems, the presence of atomically flat interfaces is essential.

Two deposition techniques have obtained from this point of view very good results, MBE and RHEED assisted Pulsed Laser Ablation. In particular, using PLA techniques [19], $\text{BaCuO}_2/\text{SrCuO}_2$ and $\text{BaCuO}_2/\text{CaCuO}_2$ superlattices have been

deposited with atomically sharp interfaces and critical temperatures as high as 70 and 80 K, respectively. It is important to stress that BaCuO_2 is not stable in bulk form even under high pressure, and that the only way to obtain it, is by depositing thin films on suitable substrates. On the other hand, CaCuO_2 and SrCuO_2 , when deposited alone as thin film, are insulators [21]. The obtained high values of critical temperatures in these superlattices are a strong evidence of the validity of the charge transfer picture for HTS compounds. Moreover, the T_c dependence upon the thickness layer of the active blocks (the CaCuO_2 and the SrCuO_2), see Fig. 3 for the case of $\text{BaCuO}_2/\text{CaCuO}_2$ superlattices, shows a maximum at which the optimal doping of the superconducting planes is reached, and decreases rapidly for larger and smaller thickness values, in a way very similar to that observed in the case of substituted HTS compounds.

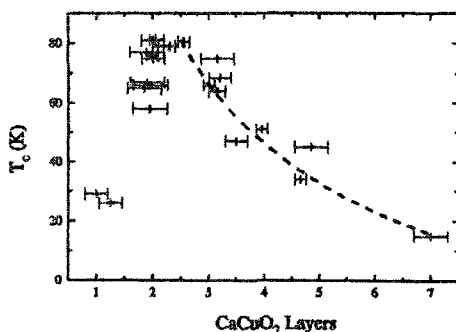


Figure 3. Critical temperature behavior versus the number of CaCuO_2 layers in $\text{BaCuO}_2/\text{CaCuO}_2$ superlattices [19].

can be naturally explained if the Cu-O_2 superconducting planes in the system are those in the CaCuO_2 blocks (about 3 Å apart) and no more those in the 2201 block (12 Å apart) [20].

Similar behavior is observed also for $\text{Bi}_2\text{Sr}_2\text{CuO}_x/\text{CaCuO}_2$ fabricated by MBE [20], in which the charge reservoir block is given by the metallic 2201 layers. In this case the doping of the CaCuO_2 layers and their nature of active blocks is confirmed by very low anisotropy measured in these superlattices. In fact, anisotropy should in principle increase going from single films to layered systems if everything else remains the same. The low anisotropy in

$\text{Bi}_2\text{Sr}_2\text{CuO}_x/\text{CaCuO}_2$ superlattices

5 HTS multilayer applications: first results and perspectives

As seen in the previous sections, the developments in the layer-by-layer deposition have opened new perspectives for atomic engineering of HTS oxide structures [5]. The interest of the research groups, originally devoted almost exclusively to HTS materials, due to the richness of behaviors shown by the class of perovskitic oxides, has spread over many compounds with different functional properties such as ferroelectricity, magnetism, metallic and semiconducting conductivity [21].

The integration of various oxides having different functional properties in a single heteroepitaxial structure is of enormous interest for practical applications. This is particularly true for the case of ferroelectric oxides, showing many physical

properties connected with their spontaneous polarization, such as the piro- and piezo-electricity, which are currently used in many sensors and actuators. Presently, many efforts in this area are addressed to the realization of alternative solutions for computer memories, using nonvolatile ferroelectric devices. Artificial ferroelectric structures have been realized by sequential deposition of ultrathin layers of different compounds, using deposition techniques similar to those developed for HTS oxides [22]. Integrated systems with ferroelectric and superconducting oxides have also been realized, improving the structural quality of the interfaces and therefore the fatigue properties of the overall device [23]. Ferroelectric oxide/HTS oxide heterostructures have been used to modulate superconductivity by switching the polarization of the ferroelectric film in a stable and reversible way [23].

Another field of new possible applications is the so-called "spintronics". The basic idea of spintronics is to take advantage of the spin degree of freedom, in addition to the charge degree of freedom, for the realization of electronic devices. In such devices it is essential the presence of an electrode able to inject electrons with high degree of spin polarization. Metallic magnetic perovskitic oxides have shown higher degree of spin polarization when compared to conventional ferromagnetic metals [24]. Moreover, their use in heterostructures with HTS oxides allows the realization of epitaxial structures with very sharp interfaces. From this point of view, the class of the hole doped manganates ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) is very promising. Several studies have been performed on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ /YBCO layered structures and tunnel junctions [25]. In particular, the observation of non equilibrium superconducting phenomena in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ / SrTiO_3 /YBCO tunnel junctions have unambiguously been attributed to dynamic pair breaking effect of the spin polarized quasiparticles, allowing to measure the c axis spin diffusion length and diffusion time [25].

6 Conclusions

The realization and study of artificial HTS layered structures has been one of the most interesting research fields in the last years. The developments in deposition techniques have allowed to perform accurate analysis of such heterostructures opening the way to engineering of completely new materials.

References

1. Bednorz J. G., Muller K. A., *Z. Phys. B* **64** (1986) 189; Chu C. W. et al., *Phys. Rev. Lett.* **58** (1987) 405; Matsui Y., et al., *Jpn. J. Appl. Phys.* **27** (1988) L827.
2. See for example, *Physical Properties of High Temperature Superconductors*, ed. by Ginsberg D. M. (World Scientific, Singapore, 1989).
3. Vailionis A., et al., *Phys. Rev. B.* **51** (1995) 3097.

4. See for example, *Materials and Crystallographic of High T_c Superconductivity*, ed. by Kaldis E., NATO ASI Series E (Kluwer Academic Publisher, 1994).
5. See for example, *Proceedings of SPIE 3481: "Superconducting and Related Oxides: Physics and Nanoengineering"* (1998).
6. Triscone J. M., et al., *Phys. Rev. Lett.* **63** (1989) 1016.
7. Triscone J. M., et al., *Phys. Rev. Lett.* **64** (1990) 804; Jia C. L., et al., *Physica C* **210** (1993) 1; Contour J. P., et al., *Jpn. J. Appl. Phys.* **32** (1993) L1134.
8. Li Q., et al., *Phys. Rev. Lett.* **64** (1990) 3086.
9. Varela M., et al., *Phys. Rev. Lett.* **83** (1999) 3936.
10. Yang H. C., et al., *Phys. Rev. B* **59** (1999) 8956.
11. Radovan H. A., Ziemann P., *Physica C* **315** (1999) 1.
12. Martinez J. C., et al., *Phys. Rev. B* **61** (2000) 9162.
13. Boebinger G. S., et al., *Phys. Rev. Lett.* **77** (1996) 5417.
14. Matsushima T., et al., *Sol. State. Comm.* **76** (1990) 1201; Horiuchi K., et al., *Jpn. J. Appl. Phys.* **30** (1991) L1381; Bozovic I., et al., *Supercond. J.* **5** (1992) 19.
15. Hatano T., Ishii A., Nakamura K., *J. Appl. Phys.* **79** (1996) 2566.
16. Li Z.Z., Rifi H., Vaurès A., Megtert S., Raffy H., *Phys. Rev. Lett.* **72** (1994) 4033.
17. Virshup G. F., et al., *Appl. Phys. Lett.* **60** (1992) 2288.
18. Torrance J. B., et al., *Physica C* **291** (1989) 162.
19. Li X., Kawai T., Kawai S., *Jpn. J. Appl. Phys.* **33** (1994) L18; Norton D. P., et al., *Science* **265** (1994) 2074; Balestrino G., et al., *Phys. Rev. B* **58** (1998) R8925.
20. Salvato M., et al., *Physica C* **341/348** (2000) 1903.
21. See for example, Salama K. In *Proc. Int. Conf. "Materials and Mechanisms of Superconductivity and High Temperature Superconductors"*, ed. by Chu W. K., Chu C. W., *Physica C* **341/348** (2000).
22. Hahn C. H., et al., *Science* **269** (1995) 373 and references therein.
23. Yu W. X., et al., *Physica C* **337** (2000) 39; Ahn C. H., et al. *Science* **284** (1999) 5417.
24. Salvador P. A., et al., *Appl. Phys. Lett.* **75** (1999) 2638.
25. Worledge D. C., Geballe T. H., *Appl. Phys. Lett.* **76** (2000) 900; Yeh N. C., et al., *Phys. Rev. B* **60** (1999) 10522.

SEMI-SPHERICAL SiGe/Si-NANOSTRUCTURES GROWN BY MBE WITH *in situ* ION-BEAM ASSISTANCE

P. I. GAIDUK, J. LUNDGAARD HANSEN, A. NYLANDSTED LARSEN

*Institute of Physics and Astronomy, University of Aarhus,
DK-8000 Aarhus C, Denmark*

E-mail: gaiduk@ifa.au.dk

In this report new semi-spherical SiGe/Si nanostructures are presented. Epitaxial islands of 30 - 40 nm in base diameter and 11 nm in height, and with a number density about $6 \times 10^{10} \text{ cm}^{-2}$ were produced on (001)-Si by MBE growth of Si/Si_{0.5}Ge_{0.5} layers with *in situ* implantation of 1 keV As⁺ ions. It was found by XTEM that the islands have a complicated inner structure and consist of semi-spherical nano-layers of different SiGe composition. Their nature and possible applications are discussed.

A self-assembly of Ge and SiGe quantum dots (QDs) on Si has attracted much attention in recent years. One of the main problems of the fabrication of Ge QDs is a relatively large size of Ge islands grown on Si in the Stranski-Krastanov mode. Several methods have recently been developed to improve the situation. The most promising approaches exploit the ability of carbon [1-4] or a very thin silicon oxide layer [5,6] to change the wetting properties of the surface and to minimize the configuration energy of small Ge islands. Another possibility to grow Ge-QDs of a very small size is the use of self-patterned SiGe template layers [7], which can be produced as a result of stress-driven instability of a stressed SiGe surface. Ge dots are in this case found to be fully located on the top of the SiGe undulations [7]. However, the crucial step of this approach is the fabrication of pre-patterned template layers of nano-scale size.

We propose to use the ion implantation as a fine tool to produce the nano-patterned surface. We suggest that implantation-induced defects are effective channels for stress relaxation in Si/SiGe layers and, as a result, create the nanopatterned surface. In this work we investigate the impact of a high dose As implantation on the surface patterning during MBE growth of multilayer Si/SiGe structures. The effect of small dose implantation on the Ge QDs formation will be presented elsewhere [8].

The samples were grown in a solid source MBE machine using e-beam evaporators for Si and Ge and a build-in low energy (1 keV) ion implanter for *in situ* incorporation of As. Wafers of p-type Si (001) were used as substrates. After SiO₂ desorption from the substrate at 900°C, a 100 nm-thick Si buffer layer was grown. Six Si_{0.5}Ge_{0.5} layers of 4 nm thick and six Si layers of 4.2 nm thick were then deposited in turn at 250°C. During the growth of the first two SiGe/Si periods the implantation of 1 keV As⁺ was *in situ* proceeded at a current density about $0.2 \mu\text{A}/\text{cm}^2$ to the total dose $3 \times 10^{15} \text{ cm}^{-2}$. Typical growth rates were $0.04 \text{ \AA/s}$ both

for Si and $\text{Si}_{0.5}\text{Ge}_{0.5}$ layers. The sample surfaces were studied by atomic force microscope (AFM). The structure of the layers was finally investigated by transmission electron microscopy in plan-view (PVTEM) and cross-section (XTEM) modes.

Fig. 1 shows the surface morphology of the sample grown in the above mentioned conditions. The formation of a high density of islands on the surface is clearly seen. The islands are of nearly spherical shape with an aspect ratio H/D (D – diameter in the base and H – height of the islands) of about 0.3 - 0.2. It can be concluded from the AFM image that the islands are rather homogeneous in size and height and have nearly round shapes in their base. The density of the islands as determined from AFM is $(6-8) \times 10^{10} \text{ cm}^{-2}$.

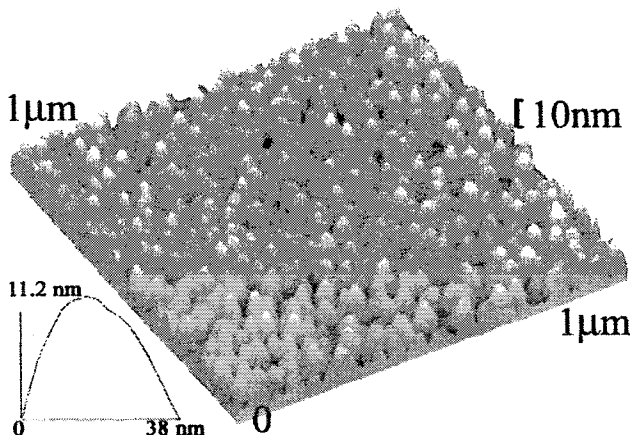


Figure 1. AFM image of SiGe/Si islands MBE grown on (001) Si. Six pairs of $\text{Si}_{0.5}\text{Ge}_{0.5}$ (4 nm) and Si (4.2 nm) layers were deposited in turn at 250°C. The first two pairs of layers were grown with *in situ* ion implantation of As^+ . The inset (bottom left) shows the result of a height scan of one typical island.

The nature of the above islands can be elucidated from TEM investigations. Fig. 2 illustrates typical PVTEM images and diffraction pattern obtained from the surface region of the sample. Bright-field PVTEM image (not shown here) reveals the existence of a strong grain contrast. The diffraction pattern (Fig. 2 (B)) contains supplementary spots of lower intensity which indicate formation of micro-twins in the layer. The dark-field PVTEM images presented in Fig. 2 (A) and (C) were obtained in a spot which originated from the diffraction on the twins and therefore reflect the size and shape of the twin particles. It is well seen from the figure that the micro-twins are faceted along $\{111\}$ planes and a typical plan-view size of the particles is about 30-40 nm which correlates well with the AFM data.

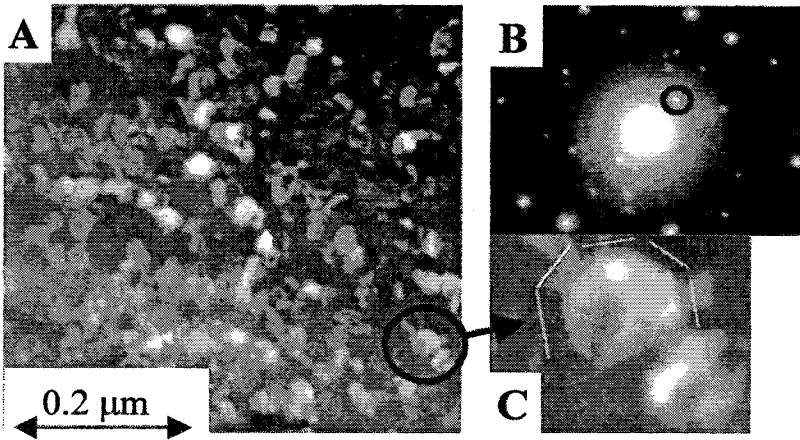


Figure 2. (A) - Dark-field TEM image of the surface layer obtained in one of the micro-twin spots as indicated on the diffraction pattern (B). The enlarged image (C) illustrates strong (111)-faceting of the micro-twin particle.

An interesting information on the inner structure of the islands is obtained from XTEM investigations (Fig. 3). It appears in particular that the islands nucleate as a small twin embryos at the second pair of SiGe-Si layers and spread out towards the surface within the sectors limited by inclined (111) planes. The twins appear to constitute the regions of enhanced crystal growth resulting in strong patterning of the surface. Another very important feature of the inner structure of the islands is that the layers of Si and Si_{0.5}Ge_{0.5} are confined in the islands as thin circular arcs distributed around the twin embryo. Such semi-spherical layers may probably influence the carrier confinement and determine electronic and optical properties of the layers.

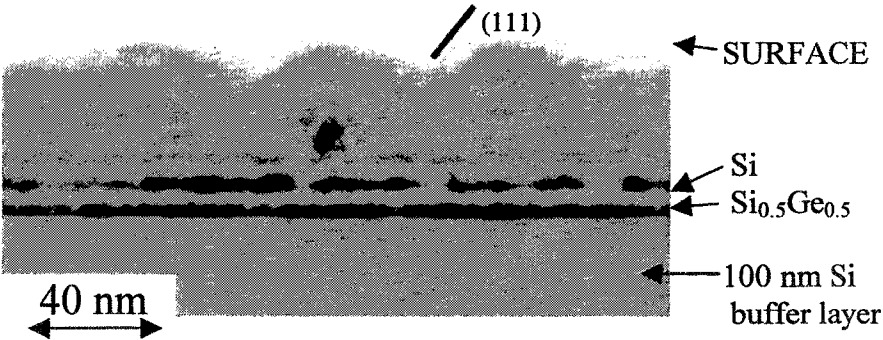


Figure 3. XTEM image of SiGe/Si islands MBE grown on (001) Si.

The stress accumulation during the growth of strained SiGe of over-critical thickness mostly results in a large-scale surface patterning [9,10]. It is expected that the implantation introduces a huge number of defects. They are usually become an effective additional channel for stress relaxation which, finally, increases the density and decreases the amplitude of the surface roughening. The resulting patterned surface seems to be more favourable as a template for Ge QD formation. In addition, after proper annealing and a good spatial separation, the highly arsenic doped layer can probably be used as a key element for the production of p-i-n⁺ structure which is expected to be a promising candidate for optoelectronic devices.

In conclusion, it has been demonstrated that MBE of Si/Si_{0.5}Ge_{0.5} layers with *in situ* implantation of 1 keV As⁺ ions results in the formation of semi-spherical SiGe/Si nanoislands of a new type. The islands have a complicated inner structure and consist of the semi-spherical nanolayers of different SiGe composition. The above surface patterning is explained by the formation of micro-twins related to stress relaxation through implantation induced defects.

References

1. Schmidt O. G., Eberl K., Multiple layers of self-assembled Ge/Si islands, *Phys. Rev. B* **61** (2000) pp.13721-13729.
2. Eberl K., Schmidt O. G., Kienzle O., Ernst F., Preparation and optical properties of Ge and C-induced Ge quantum dots on Si, *Thin Solid Films* **373** (2000) pp.164-169.
3. Leifeld O., Beyer A., Muller E., Kern K., Grutzmacher D. Formation and ordering effects of C-induced Ge dots grown on Si (001) by MBE, *Mat. Sci. & Eng. B* **74** (2000) pp.222-228.
4. Wakayama Y., Gerth G., Werner P., Gosele U. Structural transition of Ge dots induced by submonolayer carbon on Ge wetting layer, *Appl. Phys. Lett.* **77** (2000) pp.2328-2330.
5. Shklyayev A. A., Shibata M., Ichikawa M. High density ultrasmall epitaxial Ge islands on Si(111) surfaces with a SiO₂ coverage, *Phys. Rev. B* **62** (2000) pp.1540-1543.
6. Barski A., Derivas M., Rouviere J. L., Buttard D., Epitaxial growth of germanium dots on Si(001) surface covered by a very thin silicon oxide layer, *Appl. Phys. Lett.*, **77** (2000) pp.3541-3543.
7. Berbezier I., Abdallah M., Ronda A., Bremond G. Fabrication of self-patterned SiGe template layer, *Mat. Sci. & Eng. B* **69-70** (2000) pp.367-373.
8. Gaiduk P. I., Larsen A. Nylandsted, Hansen J. Lundsgaard. Will be presented at EMR-2001.
9. Shiryayev S. Y., Jensen F., Wulff Petersen J., Hansen J. Lundsgaard, Larsen A. Nylandsted, *J. Cryst. Growth* **157** (1995) pp. 132-138.
10. Gao H., Nix W. D. Surface roughening of heteroepitaxial thin films, *Annu. Rev. Mater. Sci.* **29** (1999) pp.173-209.

MOLECULAR BEAM EPITAXIAL GROWTH AND PHOTOLUMINESCENCE STUDIES OF InAs SELF-ORGANIZED QUANTUM DOTS ON PATTERNED GaAs (001) SUBSTRATES

B. C. LEE¹, H. M. LEE², J. C. WU², Y. P. CHANG³, K. W. SUN³, C. P. LEE¹

¹*Department of Electronics Engineering and Institute of Electronics
National Chiao Tung University, Shin Chu, Taiwan, Republic of China*

²*Department of Physics, National Changhua University of Education
Changhua, Taiwan, Republic of China*

³*Department of Electronic Engineering, Feng Chia University
Taichung, Taiwan, Republic of China*

E-mail: kwsun@fcu.edu.tw

We present experimental results on the growth of InAs self-organized quantum dots on patterned substrates via molecular beam epitaxy. Luminescence spectra of these quantum dots have been studied.

1 Background

There have been increasing interest in the study of self-organized quantum dot (SOQD) formation on patterned substrates to improve position control. Selective formation of InAs SOQDs on patterned GaAs substrates using chemical beam epitaxy to spatially control the positioning and alignment of SOQDs have been reported in [1-5]. The GaAs substrates were patterned by conventional lithography using SiO₂ as a mask material. By reducing the stripe top width below 100 nm, three rows, two rows, and one row of dots can be obtained [5].

In this paper we report chain formation of InAs SOQDs on a pre-patterned GaAs (001) substrate via e-beam lithography, chemical wet etching and molecular beam epitaxy. We have studied the growth behavior and optical properties of SOQDs grown on grid patterns with two different orientation angles with respect to the (100) facet.

2 Molecular beam epitaxy growth of InAs SOQDs

In the formation of SOQDs, two square grid patterns about 80x80 μm^2 were first defined on a flat (001) GaAs substrate via e-beam lithography followed by chemical wet etching. Fig. 1 shows the schematics of the grid pattern defined on the GaAs substrate. The GaAs substrate was first covered with photoresist, and then exposed to an e-beam to define the patterns. Grid patterns with stripes oriented at angles of 0, 90 deg (pattern A) and 45, 135 deg (pattern B) with respect to the (100) facet

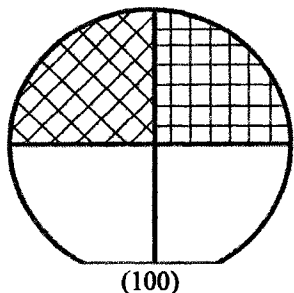
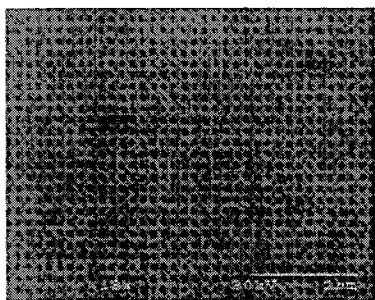


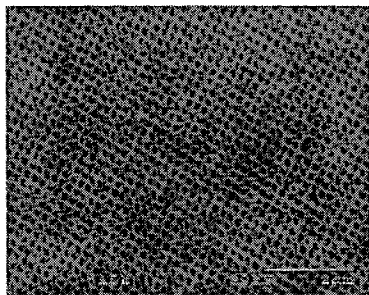
Figure 1. Schematics of the patterns defined on the GaAs substrate.

with pitch of $0.1\ \mu\text{m}$ were etched into the substrate resulting in pits with side walls of (100), (T00), (010), (0T0) facets for pattern A and (100), (T00), (110), (1T0) facets for pattern B. The pits formed had depths of about $100\ \text{\AA}$.

Fig. 2 shows the scanning electron microscope (SEM) images of the grid patterns after the chemical wet etching. The etching processes were anisotropic on the two different directions resulting in pits with a rectangular shape. Therefore, the upper and the lower pits are separated by a thinner wall than those pits sit side by side as shown in the SEM images.



(a)



(b)

Figure 2. SEM images of (a) grid pattern A (stripes are oriented at 0 and 90 deg to the (100) facet) and (b) grid pattern B (stripes are oriented at 45 and 135 deg to the (100) facet) after chemical wet etching.

The molecular beam epitaxial growth sequence consisted of 1.42 monolayer of InAs at $500\ \text{\AA}$ after the growth of $100\ \text{\AA}$ buffer layer on the patterned substrate. The SOQDs were formed on both patterned and non-patterned area. The Atomic force microscopy (AFM) image of the SOQDs formed on the non-patterned area is shown in Fig. 3. The SOQDs so formed are distributed in a random manner and exhibit fluctuations in size.

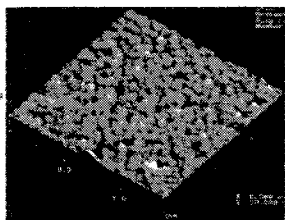


Figure 3. AFM image of the uncapped SOQDs on the non-patterned area with 1.4 ML of nominal InAs deposition.

In Fig. 4, we have shown AFM images taken from the center of the pattern A. The stripes parallel to the (010) facet and have top widths about $50\ \text{nm}$. The inset in Fig. 4 shows only one row of SOQDs formed on those stripes. The dots landed on the stripes have an average base width about $300\ \text{\AA}$ and are more uniform in size than dots formed on the non-patterned area. We found no dots formed on those stripes parallel to the (100) facet due to much narrower top widths (much less than the widths of the dots).

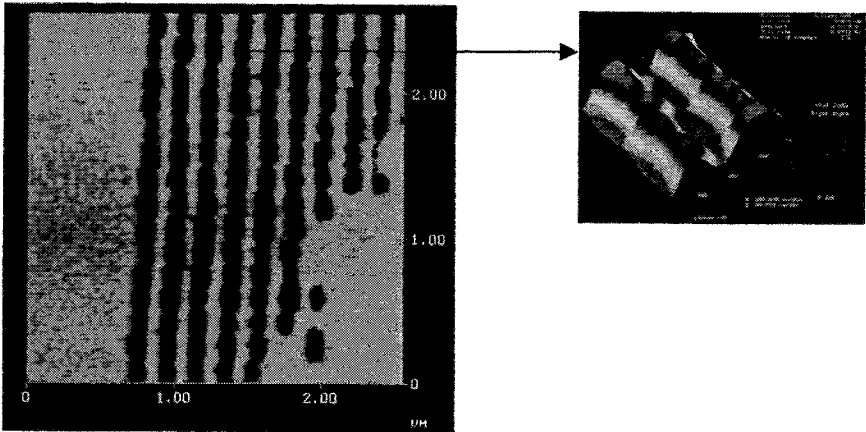


Figure 4. AFM images of SOQDS grown on the pattern A. The inset shows one row of dots landed on the stripes.

The AFM images taken from the pits are also shown in Fig. 5. The inset in this figure indicates that there is also one row of dots formed inside the pit. The position of these dots landed inside the pits looks asymmetric with respect to the center of the pits. We are currently investigating this issue. We have also found that the density of SOQDs formed on pattern A is significantly higher (about $3 \times 10^{10} \text{ cm}^{-2}$) than those formed on the non-patterned area and pattern B (about $4 \times 10^9 \text{ cm}^{-2}$).

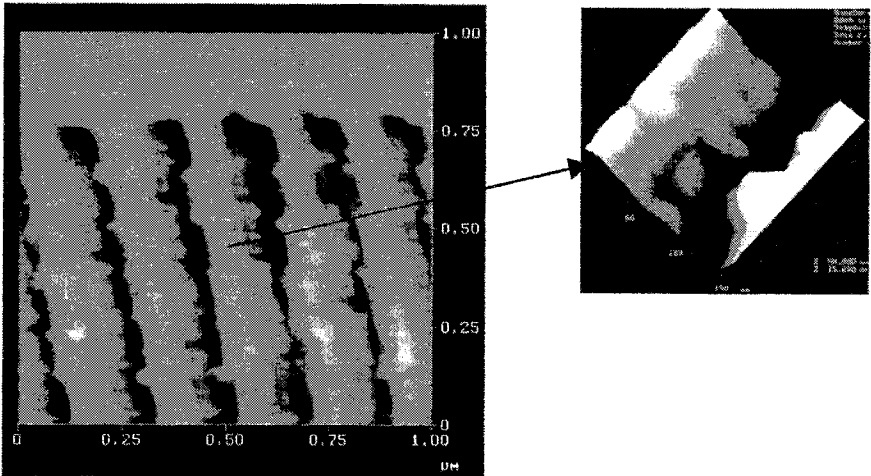


Figure 5. AFM images of SOQDS inside the pits of pattern A. The inset shows one row of the dots sitting against the (010) facet.

3 Photoluminescence studies of quantum dots

We have recorded photoluminescence spectra of the SOQDs formed on the pattern A, B and non-patterned area at low temperature. In the photoluminescence experiments, the sample was excited with an Ar^+ laser operated at $\lambda = 514.5 \text{ nm}$. The laser was focused to a spot size of approximately $60 \mu\text{m}$ in diameter (to cover only the patterned area) with 5 mW of average power. The sample was kept in a closed-cycled refrigerator at about 15 K. The image of the sample was first magnified in order to direct the laser beam onto the patterned area through a periscope arrangement behind the entrant slit of the spectrometer. The luminescence was then collected and analyzed with a combination of $0.6 \mu\text{m}$ triplemate spectrometer and a liquid-nitrogen cooled CCD camera.

In Fig. 6 we have shown the photoluminescence spectra of the SOQD sample taken from the three different regions: pattern A, non-patterned area and pattern B. The SOQDs grown on pattern A gave the strongest PL intensity among them. We attribute this to the improvement of the dot size uniformity and the higher density of SOQDs formed in this area. The luminescence peak in the spectrum has also shown a large blue-shift in comparison to the luminescence signal from the non-patterned area. For SOQDs grown on pattern B, the luminescence intensity is approximately the same as for the non-patterned area. However, its peak is slightly blue-shifted in comparison to the non-patterned signal, though not as significant as the peak for pattern A.

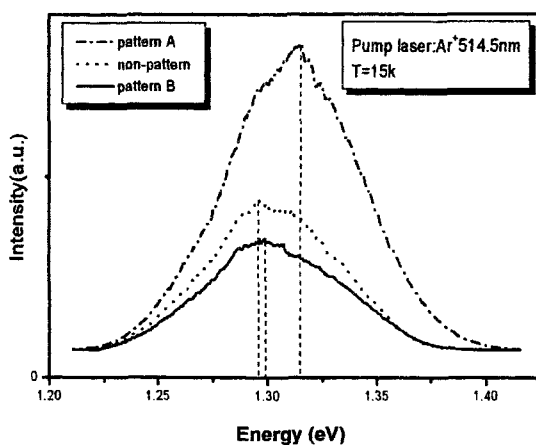


Figure 6. Photoluminescence spectra from three different areas on the sample: pattern A, non-patterned, and pattern B. The spectra were taken using a liquid nitrogen cooled CCD camera under the same excitation conditions and integration time.

4 Summary

In summary, we have grown InAs SOQDs via molecular beam epitaxy on patterned GaAs (001) substrates prepared by e-beam lithography and chemical wet etching. Our AFM images show ordering of SOQDs formed on the stripes. From the luminescence studies we found that the SOQDs grown on pattern A gave the strongest luminescence intensity among the three areas that we have investigated. We attribute this to the higher density, ordering and improvement in the size uniformity of the dots.

5 Acknowledgements

This work was supported by National Science Council of the republic of China under contract Grant No. NSC89-2112-M-035-005 and NSC89-2112-M-035-010.

Reference

1. Mui D. S. L., Leonard D., Coldren L.A., Petroff P.M., *Appl. Phys. Lett.* **66** (1995) 1620.
2. Sugiyama Y., Sakuma Y., Muto S., Yokoyama N., *Appl. Phys. Lett.* **67** (1995) 256.
3. Jeppesen S., Miller M., Hessman D., Kowalski B., Maximov I., Samuelson L., *Appl. Phys. Lett.* **68** (1996) 2228.
4. Kamins T., Williams R., *Appl. Phys. Lett.* **71** (1997) 1201.
5. Zhang R., Tsui R., Shiralagi K., Convey D., Goronkin H., *Appl. Phys. Lett.* **73** (1998) 505.

PRODUCTION TYPE PLANETARY® MOVPE REACTORS FOR FABRICATION OF NITRIDE QUANTUM WELL LASERS

B. SCHINELLER, H. PROTZMANN, M. LUENENBUERGER, M. HEUKEN

AIXTRON AG

Kackertstr. 15-17, D-52072 Aachen, Germany

E-mail: bschi@aixtron.com

E. V. LUTSENKO, G. P. YABLONSKII

Stepanov Institute of Physics, National Academy of Sciences of Belarus

F. Skaryna Ave. 68, 220072 Minsk, Belarus

E-mail: yablon@dragon.bas-net.by

We have developed the AIX 2000 G3 HT MOVPE machine for large scale production of nitride semiconductors. Extensive numerical modeling of the reactor chamber has enabled us to establish process windows for the growth of nitride quantum wells. We report excellent wafer-to-wafer, on wafer and run to run uniformities across all wavelength regions accessible to the InGa_N material system. Laser action in GaN epitaxial layers and InGa_N/GaN quantum well heterostructures at optical excitation was achieved in the spectral range from 370 nm to 470 nm. The working temperature reached 580 K for the best multiple quantum well structures.

1 Introduction

Nowadays nitride semiconductors are widely used for display and lighting applications in the spectral range from green to UV [1,2]. However, in the recent years a special focus of researches has been aimed of the commercialization of nitride blue laser diodes for optical storage and laser television. Paramount issue of such commercialization is large scale reproducible production of nitride semiconductor layers. Metal organic vapor phase epitaxy (MOVPE) has established itself as the layer growth method of choice for modern semiconductor layers. AIXTRON's AIX 2000 G3 HT family was developed to meet the needs of modern production facilities by low overall running costs and low cost of ownership while maintaining high standards for yield affecting issues like wavelength uniformities on a wafer and from wafer to wafer and from run to run.

2 Experimental and results

Fully loaded growth runs were performed in an AIX 2000 G3 HT reactor in the 6 x 2 inch configuration using triethylgallium (TEGa), trimethylgallium (TMGa),

trimethylindium (TMIn), ammonia (NH_3), silane (SiH_4), biscyclopentadienyl-magnesium (Cp_2Mg) as precursors and H_2 and N_2 as carrier gases. C-plane sapphire wafers were used as substrates. The reactor total pressure for the growth of the buffer and quantum well structures was kept constant at 200 mbar throughout the process. A conventional low temperature GaN nucleation layer with the subsequent anneal step was grown prior to the high temperature buffer growth at 1170 °C. To establish basic growth mechanisms and process parameters for the growth of InGaN quantum wells and GaN barriers numerical heat transfer and fluid dynamic simulations were performed employing a finite volume method.

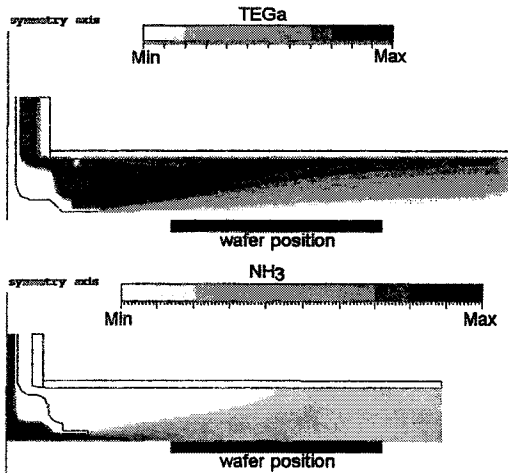


Figure 1. Numerical simulations for NH_3 (lower) and TEGa (upper) mass flows inside the reactor chamber for $T_D = 800$ °C, $P_{\text{tot}} = 200$ mbar and $Q_{\text{tot}} = 28$ slm. Symmetry axis of the reactor chamber and inlet are on the left hand side, direction of gas flow is from left to right.

The results of theoretical simulation presented in Fig.1 show that a homogeneous depletion zone above the wafer can be achieved with 28 slm at 200 mbar at a growth temperature around 800 °C. These conditions were used as starting parameters for the experimental optimization. Ten period multi-quantum well (MQW) structures were grown with varying parameters such as temperature and ratio between hydride and IIIa-compounds flow.

Fig. 2 (right) exhibits the distribution of the layer thickness from wafer to wafer for all six wafers from the same run. Standard deviation of 0.7 % can be reached indicating a well tuned linear decrease of the growth rate above the rotating wafer disk. This thickness homogeneity is also reflected in the thickness-dependent peak of the room temperature photoluminescence (PL). In this case wafer-to-wafer standard deviations of 0.9 % at 440 nm, 1.4 % at 470 nm, 1.3 % at 500 nm and 0.3 % at 580 nm could be achieved. The relatively high standard deviation of the wavelengths in the medium spectral range is attributed to the miscibility gap of the In-Ga-N system which becomes extremely susceptible to temperature deviations. InGaN emitting in the low and high energy spectral ranges tends to have a more

defined composition as the miscibility gap shrinks towards the In-rich and Ga-rich compositions.

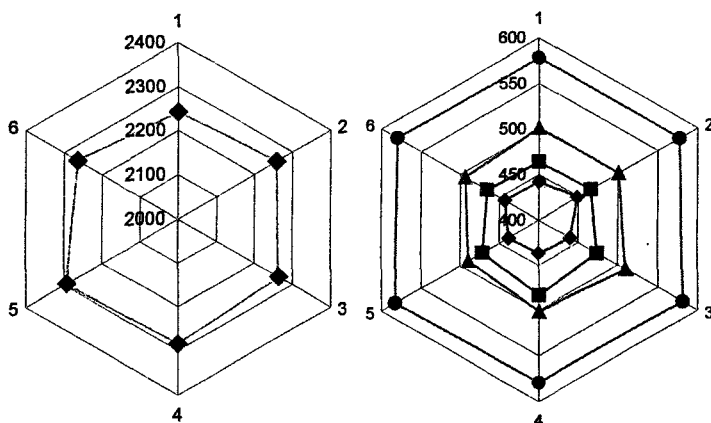


Figure 2. Spiderweb results on wafer to wafer reproducibility for total thickness (left) and wavelength (right, for different process conditions). The azimuthal position describes the load position of the wafer.

Fig. 2 (left) shows the total layer thickness measured by white light interference for a set of samples grown in the same run. The standard deviation of 0.7 % in layer thickness at an average thickness of 2.7 μm is a proof of the high wafer-to-wafer uniformity which is of paramount interest in the growth of quantum well structures.

With these prospects we have investigated the lasing properties of these samples. On the way to the development of new laser structures the investigation of optically pumped lasers and PL are the fastest methods for the layer quality characterization and for the elucidation of the optimal growth conditions and structure design [3,4].

Laser-stimulated emission (SE), PL spectra and emission intensities of GaN epitaxial layers, InGaN/GaN single and double heterostructures (SH, DH), single and multiple quantum wells (SQW, MQWs) were investigated as a function of the structure design and the N_2 laser excitation intensity (I_{exc}) ($h\nu=3.68$ eV, $f=1000$ Hz, $t=8$ ns, $I_{\text{exc}}=10^2\text{--}10^6$ W/cm²) in the temperature range from 78 K to 500 K. The angular dependence of the spectral distribution of the laser emission was monitored in the plane perpendicular to the heterostructure using an optical fiber system in the edge geometry for both polarizations. The output-input characteristics revealed a very fast rise of the emission intensity near the threshold for the TE polarizations. An appearance of the far-field pattern and very narrow laser lines at the threshold intensities were observed for all structures. Laser action in GaN epitaxial layers and InGaN/GaN quantum well heterostructures was achieved in the spectral range from 370 nm to 470 nm. The wavelength of the lasers was changed by the In content in the active layers and by their thickness alteration from several tens up to several

nanometers. The working temperature reached 585 K for the best structures consisting of 10 QWs with InGaN layer thickness about 10 nm.

The value of the lasing threshold increased from 50 kW/cm^2 to 800 kW/cm^2 with an increased operating wavelength of the MQW lasers owing to the In rich cluster and defect formation at high In concentration in the InGaN active layers. The maximum energy and power per pulse of the MQW laser were 100 nJ and 12 W, respectively, for one facet at room temperature.

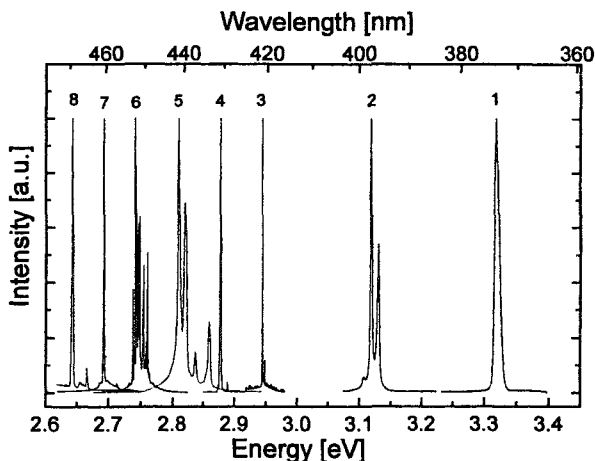


Figure 3. Laser spectra of GaN epitaxial layer (1), InGaN/GaN single (2) and multiple (3-8) quantum well heterostructures at 300 K.

Fig. 3 shows the laser spectra of different types of the GaN based heterostructures measured at room temperature. It has been established that the gain mechanism in the GaN layers in the temperature range from 4.2 K to 300 K was recombination in a high density electron hole plasma appearing after overcoming the threshold value of the Mott transition. The laser action in the InGaN/GaN QW lasers operating in the violet region (390-440 nm) was reached only after saturation of the recombination transitions via the deep states attributed to the inhomogeneously distributed In-rich clusters. The wavelengths of these lasers are near to the mobility edge of the active InGaN layers. It was shown that the quantum energy of the laser emission in the blue lasers (450-470 nm) was less than the band gap energy of the active layers. It has been supposed that the laser action in blue spectral region takes place due to recombination via the bound states connected with In-rich clusters (quantum dots or discs) inside the InGaN active layers.

3 Summary and conclusions

We have investigated the growth parameters for the uniform formation of InGaN/GaN MQW structures in an AIX 2000 G3 HT MOVPE machine by numerical simulation of the reactor chamber and experimental optimization. Good wafer-to-wafer and run-to-run reproducibilities were achieved over the whole spectral range accessible to InGaN heterostructures. The lasing was achieved over a wide spectral range up to wavelengths of 470 nm and temperatures of up to 580 K. This emission is believed to be attributable to electron-hole recombination inside In-rich clusters localized inside the quantum wells. We conclude that the AIX 2000 G3 HT MOCVD machine is an excellent tool for mass production of laser structures with respect to wafer uniformity which is precondition for a high yield.

4 Acknowledgements

We thank I. P. Marko, V. N. Pavlovskii and V. Z. Zubjalevich for their assistance. The work was partly supported by the Belarus-INTAS project 97-0995.

References

1. Nakamura S., Senoh M., Nagahama S., Matsushita T., Kiyoku H., Sugimoto Y., Kozaki T., Umemoto H., Sano M., Mukai T., Violet InGaN/GaN/AlGaIn based laser diodes operable at 50°C with a fundamental transverse mode, *Jpn. J. Appl. Phys.* **38** (1999) pp. L226-L229.
2. Yamada T., Applications of short wavelength laser diodes in future optical disk systems, presented at the *Intern. Conf. On Silicon Carbide, TTT-Nitrides and Related Materials* (Stockholm, Sweden, 1997).
3. Marko I. P., Lutsenko E. V., Pavlovskii V. N., Yablonskii G. P., Schön O., Protzmann H., Lünenbürger M., Schineller B., Heime K., High-temperature lasing in InGaN/GaN multiquantum well heterostructures, *Phys. Stat. Sol. (b)* **216** (1999) pp. 491-494.
4. Yablonskii G. P., Lutsenko E. V., Marko I. P., Pavlovskii V. N., Mudryi A. V., Stognii A. I., Schön O., Protzmann H., Lünenbürger M., Schineller B., Heuken M., Heime K., Stimulated emission, electro- and photoluminescence of InGaN/GaN EL-test and SQW heterostructures grown by MOVPE, *Phys. Stat. Sol. (a)* **180** (2000) pp. 149-155.

SPM MODIFICATION OF ORGANIC LANGMUIR-BLODGETT FILMS

L. V. KUKHARENKO, V. G. LESCHENKO

*Minsk State Medical Institute
Dzerzhinskii Ave. 83, 220116 Minsk, Belarus*

G. Y. AKULOV

*Institute of Solid State and Semiconductors Physics
P. Browka Str. 17, 220072 Minsk, Belarus*

V. M. ANISHCHIK, V. V. GRUSHEVSKI, G. V. KRYLOVA, A. I. KHMELNITSKI

*Belorussian State University
F. Skaryna Ave. 4, 220050 Minsk, Belarus*

E-mail: luda@iftp.bas-net.by

Different methods of nanostructure fabrication with scanning probes are reported. We show square holes and more complex patterns created on dithienylpyrrole Langmuir-Blodgett films. The shape of nanostructures is found to be strongly dependent on the film morphology and formation methods.

1 Introduction

In the last decade, considerable interest has grown in nanostructure fabrication on organic Langmuir-Blodgett (LB) films by various scanning probe techniques [1-3]. Scanning probe microscope (SPM) has been proven to be a powerful tool not only for imaging, but also for modification of the LB film surface with nanometer-scale resolution.

In this paper, we present results of surface investigation of dithienylpyrrole LB films by multimode SPM. Different methods for controlled and reproducible modification of the films with AFM and STM are considered.

2 Experimental procedures

The dithienylpyrrole LB films (Y-type) were prepared by usual LB technique onto freshly cleaved highly oriented pyrolytic graphite (HOPG) and mica at a deposition speed of 6.7 mm/min and surface pressure of 35 mN. Surface morphology of the films and their nanomodification were performed with SPM Solver-P47h (NT-MDT, Moscow) and FemtoScan001 (MSU, Moscow).

3 Results and discussion

Surface morphology of the films was studied with the AFM in intermittent contact. The morphology was found to change drastically with varying number of monolayers, subphase and the type of substrate employed. The film deposited on mica (three monolayers) consists of randomly connected islands with curved boundaries, similar to fractals. The surface of the seven monolayers on mica, however, possesses grain structure with the grain size ranging from 20 to 50 nm. Large grains of the order of 200 nm were observed on the film surface independent on the number of layers. These can be either FeCl_3 crystals originated from the adhesion of ubphase drop on the film surface or clusters splitted out from the film during the process of its formation at the meniscus from a monolayer on the subphase surface. It has been just the phase images and the adhesion force map that allow us to conclude that these large grains are clusters of amphiphilic molecules.

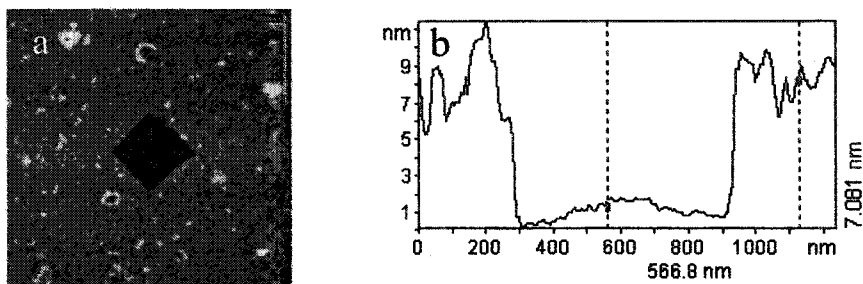


Figure 1. (a) AFM image (height, contact mode) of dithienylpyrrole LB film on mica (3 monolayers, $\text{Fe}(\text{NO}_3)_3$ subphase) with a written square hole. (b) Profile along the line cutting through the hole.

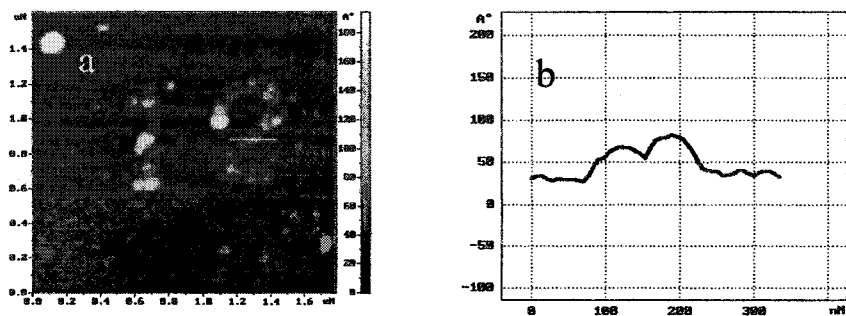


Figure 2. (a) AFM image (height, intermittent contact) of dithienylpyrrole LB film on mica (7 monolayers, FeCl_3 subphase) with a written figures "1" and "2". (b) Profile along the line cutting through the written figure "2".

In the AFM image, shown in Fig. 1(a), a well defined square hole 610x610 nm in size can be clearly seen which has been formed by increasing the force to 70 nN. Similar structures can be formed in a sequence. A contamination of the AFM probe

by the film material could lead to formation of irregular holes and correspondingly to destruction of periodicity. The modification was performed otherwise (see Fig. 2(a)) by increasing the force on the cantilever (Si, $k = 48$ N/m), but the intermittent contact of the AFM operation had been chosen and the tip motion occurred under a preset program. If in the first case we observed the square hole ~ 7 nm in depth (Fig. 1(b)), roughly corresponding to the height of three monolayers, then in the second one the written figures "1" and "2" appeared as convex up and, most likely, has been formed by grains of the amphiphilic dithienylpyrrole molecules. The dimensions of the written figure "2" are ~ 8 nm in height and ~ 15 nm in width (Fig. 2(b)).

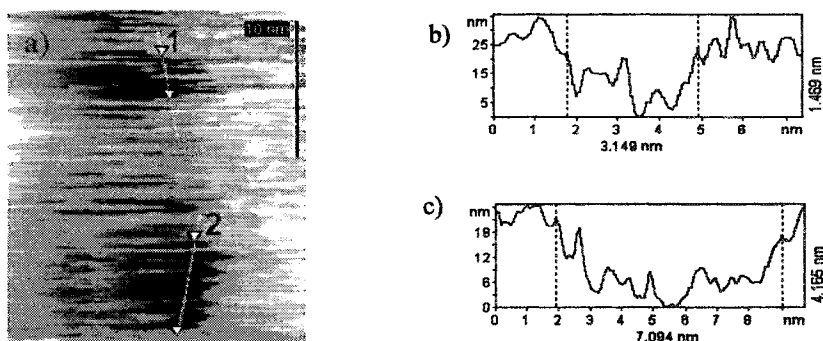


Figure 3. (a) STM images of dithienylpyrrole LB film on HOPG, (4 monolayers, FeCl₃ subphase) after applying the bias of 5V. (b) and (c) - profiles along the lines (1, 2) cutting through the formed holes.

The surface morphology of the LB films deposited on HOPG did not change depending on the number of monolayers. The films were composed of randomly connected islands with curved boundaries. In Fig. 3(a), an STM image is given for a four layer LB film surface modified under the action of electron beam. Applying the bias of 5 V between the substrate and the tip, a hole formation of 3-7 nm in diameter is visible (Fig. 3(b)). Figures "1", "1", "1" (Fig. 4) were written with AFM under different conditions, namely, in the contact mode without applying the voltage and in the contact mode with the bias of 5 V and 10 V between the tip and the substrate. Figure "1" which is clearly seen in the C-position of the scan area has been written in the contact mode (10 V). The same figure "1" in the B-position of the scan area was obtained with the bias of 5 V is less distinct. Figure "1" (practically invisible) in the A-position of the scan area has been written by change of the force acting on the cantilever with no voltage. The emergence of figure "1" of 6-7 nm in depth and 40-50 nm in width in the C-position can, obviously, be interpreted by the destruction of the LB film under the action of the beam of electrons emitted from the tip when a high electric field was applied between the tip and the substrate. Upon applying 5 V along with partially destruction of the LB film, probably, its polymerization occurs.

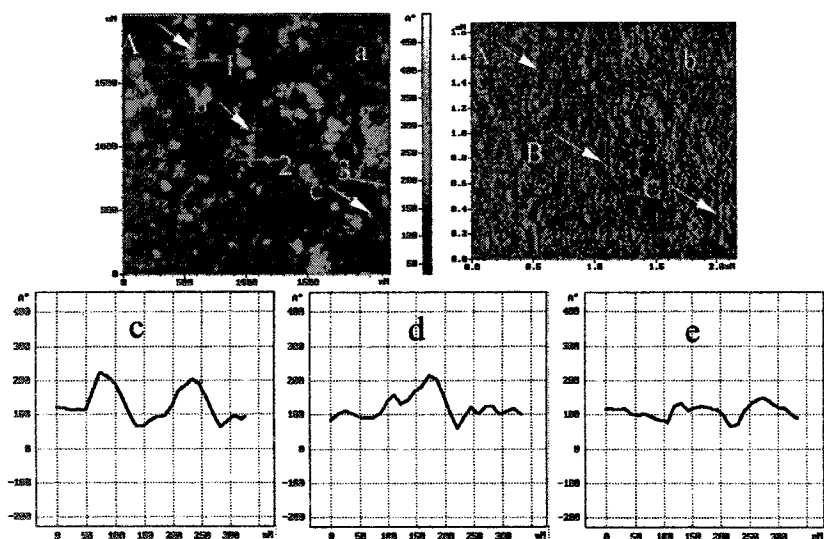


Figure 4. AFM image (a - height, b - phase) of dithienylpyrrole LB film on HOPG (6 monolayers, FeCl_3 subphase) with written figures "1", "1", "1". (c), (d), (e) - profiles along lines (1, 2, 3) cutting the formed figures.

In conclusion, the shape of the nanostructures is strongly dependent on the LB film morphology and formation methods. The methods demonstrated are versatile and powerful tools to create complex nanometer-scale structures.

4 Acknowledgements

The authors are very thankful to Prof. V. A. Bykov and Dr. A. Alexeev for providing the equipment for carrying out the experiments. This research was supported by Basic Research Foundation of Belarus (Grant № T99-227).

References

1. Solonovich V. K., Kukharensko L. V., Some local structure regularities of bicomponent Langmuir-Blodgett monolayers obtained on an STM. In *Mater. of the Second International Conf. on Nanometer Scale Science and Technology*, (Moscow, Russia, 1994) pp. 288-295.
2. Kim J. C., Lee Y. M., Kim E. R., *Thin Solid Films* **327** (1998) 690.
3. Maruyama H., Kosai N., Nanometer-scale hole- and bit-modifications of oligosilane and stearic acid Langmuir-Blodgett films, *Thin Solid Films* **338** (1999) pp. 155-160.

ADVANCING MAGNETIC FORCE MICROSCOPY

I. FEDOROV, V. SHEVYAKOV

*Moscow Institute of Electronic Engineering
103498 Moscow, Zelenograd, Russia*

E-mail: fedorov_work@newmail.ru

P. PRIKHODKO

*Moscow Institute of Physics and Technology
141700 Moscow Region, Dolgoprudnyi, Russia*

E-mail: petropro@mail.ru

The work is focused on the most serious problems of MFM, connected with the development of new types of cantilevers, fabrication of calibration structures and evolution of the method itself. We present a construction of the silicon cantilever with the two-layer coating: magnetic and protective. The structures for calibration and the approach for measurements of objects with small magnetization are shown.

1 Introduction

Magnetic force microscopy (MFM) is the most useful method of Scanning Probe Microscopy (SPM) [1,2] which allows to investigate surface magnetic properties of materials with high resolution [3]. A magnetic force microscope consists of atomic force microscope and magnetic micromechanical tip (cantilever). However, the wide use of MFM is limited by three problems: cantilevers, calibration structures and measuring technique. The MFM method requires the ultrasharp, highly sensitive magnetic cantilevers and test structures for microscope and tip calibration. Moreover, MFM itself needs to be further developed.

The most widely used magnetic cantilevers are standard Si or Si₃N₄ cantilevers coated by Co, Fe, or Ni or their alloys. The choice of the cantilever and accuracy of the measured MFM image are determined by the minimal magnetic interaction between cantilever and sample surface. The disadvantages of the mentioned cantilevers are connected with their short lifetime due to oxidation of ferromagnetic coating, and big tip curvature (50-80 nm). Deterioration of the properties of a cantilever results in decrease of its spatial and magnetic resolution. In this case the protective coatings can be applied to suppress the tip oxidation process.

2 Methods

2.1 Magnetic cantilevers

We have developed a universal cantilever for any SPM investigations. It is based on the silicon cantilever with two-layer coating: magnetic (Co) and protective (TiO_{2-x} or Au). The thicknesses of the magnetic and protective layers were optimized to get the best magnetic characteristics of cantilevers.

The cantilevers were fabricated by the technology described recently in [4]. The tip curvature was found to be about 10 nm. The schematic representation of the cantilever fabrication is shown in Fig. 1.

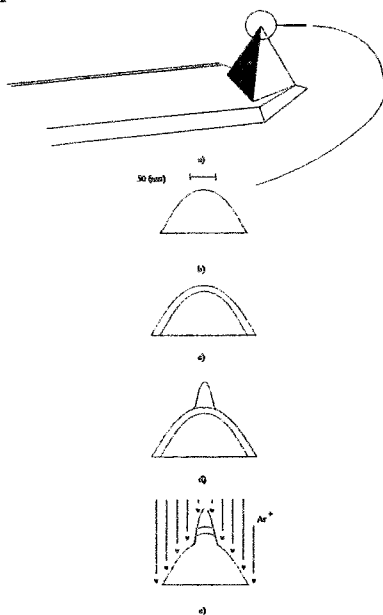


Figure 1. The schematic representation of the cantilever fabrication.

The silicon cantilevers were covered by ferromagnetic film of 50-100 nm thickness. Afterwards, it was located in SEM, where electron beam was focused on the tip apex for 10-15 min. This resulted in formation of the sharp carbon tip at the apex. The carbon tip radius was 10-15 nm. At the last step of the cantilever fabrication ion etching was performed. The etching direction was parallel to the tip. After etching the ferromagnetic material appeared to be located only under the carbon tip. Fig. 3 illustrates the use of these cantilevers in AFM and MFM measurements.

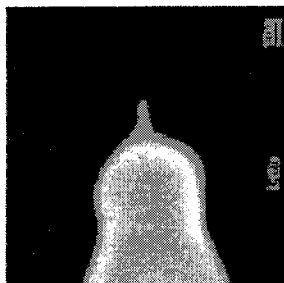
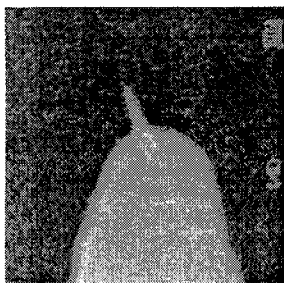


Figure 2. SEM image of a magnetic cantilever after fabrication of the carbon tip (from the two sides).

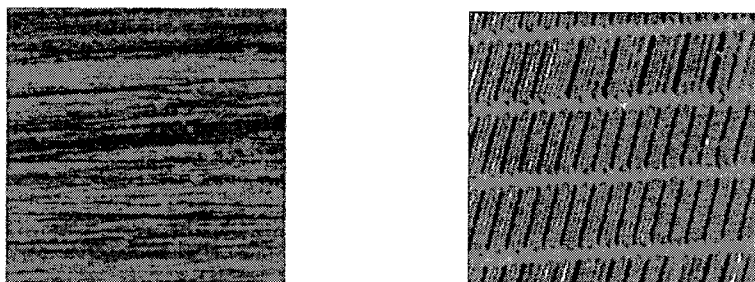


Figure 3. The AFM and MFM images ($25 \times 25 \mu\text{m}^2$) of hard disk driver acquired by cantilever with the carbon tip.

2.2 Calibration structures

We have developed and tested the three effective structures for MFM calibration. The first one consists of an oxidized silicon substrate with chaotically located ferromagnetic nanoparticles. The second structure is anodized aluminum porous film on silicon substrate with pores filled by Ni or Co. The third structure is Co nanoscale granules embedded into Cu film deposited on mica substrate.

2.3 Evolution of MFM

In order to obtain a valid MFM image, the topographic and magnetic data have to be separated. It is indeed important for objects with small magnetization and rough surface. Therefore, a magnetic component must be amplified. For this purpose we locate the sample near the source of homogeneous magnetic field.

3 Summary

We developed new types of magnetic cantilevers, calibration structures and proposed the approach for MFM measurements of objects with small magnetization. The specific details are to be discussed at the Conference.

References

1. Martin Y., Wickramasinghe H. K., *Appl. Phys. Lett.* **50** (1987) 1445.
2. Porthun S., Abelman L., Lodder J. C., *J. Magn. Magn. Matter.* **182** (1998) 238.
3. Vu L. N. et. al., *IEEE Trans. Appl. Supercond.* **3** (1997) 1918.
4. Leinebach P., Memmert U., Schelten J., Hartman U., *Appl. Surf. Sci.* **144-145** (1999) 492.

MICROPOROUS XEROGELS IN MESOPOROUS ANODIC ALUMINA

N. V. GAPONENKO

*Belarusian State University of Informatics and Radioelectronics
P. Browki 6, 220013 Minsk, Belarus*

E-mail: nik@nano.bsuir.edu.by

The paper summarises our recent results on synthesis and investigation of photoluminescence (PL) from Er and Tb doped microporous xerogel solids mesoscopically confined in porous anodic alumina. Possible mechanisms, driving the enhancement of lanthanides PL are discussed.

1 Introduction

Porous materials are investigated as a wide application area where pores of a submicron to micron order are required. Recently, we proposed to employ mesoporous materials as a template for fabricating luminescent sol-gel derived films. A sol-gel derived film could be prepared from a coatable colloidal solution which is a dispersion of colloidal particles with diameters of 1 to 100 nm in a liquid [1]. A gel has rigid network with pores submicrometer dimensions and polymeric chains whose average length is greater than a micrometer" [1]. Drying of a gel at or near ambient conditions result in removing a liquid from a gel and its shrinkage that is transferring a gel into a monolith called xerogel. The sol-gel method allow to fabricate the thin uniform films by dipping or spin-on technique on a flat surface of semiconductors, glasses and metals. Transition of a sol to a gel and then xerogel allow different soluble doping impurities to be incorporated from a sol in a xerogel matrix. Their content could be tailored within a wide range up to the concentrations comparable to those of xerogel cations. Xerogel films are widely used in industry as diffusion source in semiconductors, as well as antireflective coatings, etc [2].

Sols with a low viscosity may penetrate into mesoporous layers and fabricate there a xerogel film. It makes the method prospective while chemical content of interior surface and optical spectra of solids may be tailored. It is intriguing to extend the class of mesoporous materials giving novel optical and structural properties when coated with the xerogel films. Previously we reported on strong photoluminescence of lanthanides and modulation of refractive index in the structures xerogel/porous silicon [3], anodic alumina [4-8] or artificial opals [9]. A schematic illustration of these samples is given in Fig. 1.

Mesoporous silicon coated with Er-doped silica gel exhibited strong 1.53 μm light emission [3], that was recently confirmed in [10]. Artificial opals, consisting of silica globules, impregnated with titania xerogel, revealed a sharp band on reflection

and transmission spectra in the visible range, that we ascribed to photonic band-gap effect [9].

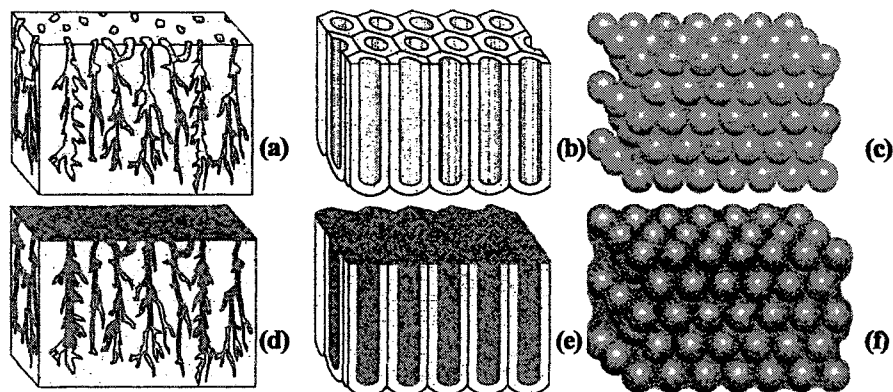


Figure 1. Schematic structures of porous silicon with a random distribution of pores (a,d), porous anodic alumina with vertical channels of the pores (b,e) and opal-like colloidal crystals with a 3D periodicity: (a), (b), (c) – uncoated samples, (d), (e), (f) – coated with xerogel film.

However, the technology of fabrication of mesoporous Si or artificial opals requires improvement because of the wide size dispersion of the pores and their orientations of the former and fragility of the latter types of matrices. It leads to non-reproducible PL intensity originating from the incorporated sol-gel derived host [11]. On the contrary, porous anodic alumina reveals a regular pore morphology with pores at the centre of approximately hexagonal cells (Figs. 1 (b,d) and 2 (a)) whose size can be tailored [12,13].

This paper summarises our investigations on synthesis and characterisation of sol-gel derived films doped with the lanthanides onto porous anodic alumina.

2 Experimental

Porous anodic alumina was fabricated by co-authors of the refs. [4-8] either on aluminium foils (UMIST, Manchester) or Al deposited onto silicon (BSUIR, Minsk) by anodising in electrolytes based on phosphoric or oxalic acids. The average pore size was ranged from 40 to 120 nm in diameter depending on the type of the electrolyte. To fabricate SiO_2 , TiO_2 , Al_2O_3 and other xerogel films doped with lanthanides different sols have been developed [14]. Most of the sols were prepared from $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Ti}(\text{OC}_2\text{H}_5)_4$ precursors containing nitrites of lanthanides, while their film products turn out to be most uniform. Typical concentration of sols was about 20-30 mg/ml. Lanthanide nitrites were dissolved in a homogeneous phase with ethanol and water to fabricate a xerogel film containing from 10 to 70 wt. % of Er or Tb oxides. The sols containing lanthanides were

deposited onto the samples by spinning at a rate ranging from 2000 to 3000 rpm or dipping technique followed by annealing. Sequential coatings were fabricated by deposition of each layer followed by drying.

3 Results and discussion

The first results related to strong room-temperature 1.53 μm emission from xerogel/anodic alumina structure we obtained in 1994 and reported in 1995 [4]. Initially porous anodic alumina of 3 μm thick and Er doped silicagel derived from $\text{Si}(\text{OC}_2\text{H}_5)_4$ were employed. Further, from the viewpoint of reproducibility the sol-gel technology, we used titania xerogels instead of silica as a host of optically active lanthanides.

Strong enhancement of Er and Tb PL from xerogel films confined in mesoporous anodic alumina was observed in comparison with spin-on films fabricated on monocrystalline Si [7]. Typical illustration of enhancement of the lanthanide PL from xerogel solids mesoscopically confined in porous anodic alumina with the size of the pores 80 nm is given by Fig. 2 (a).

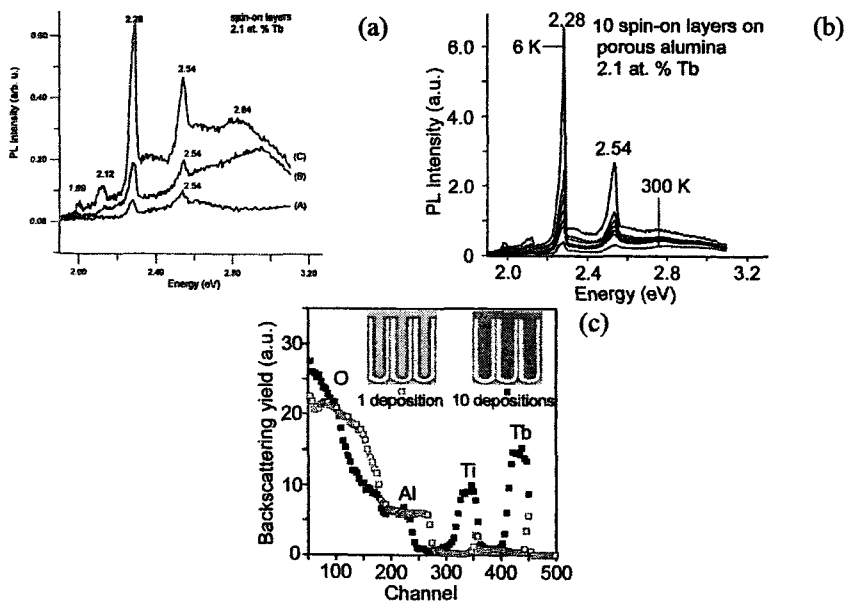


Figure 2. Characteristics of titania xerogel films doped with 2.1 at. % Tb spun-on silicon and porous anodic alumina: comparison the PL spectra of xerogels on silicon and porous anodic alumina (a), PL spectra between 300 and 6 K of ten spin-on depositions on porous anodic alumina (b), comparison the RBS data of porous anodic alumina spin-on coated with Tb doped xerogel one and ten times (c): (A) – ten spin-on depositions on silicon, (B) – one spin-on deposition on porous anodic alumina, (C) – ten spin-on depositions on porous anodic alumina (after [7]).

Schematic image of porous alumina coated with xerogel one and ten times is given by the insert in Fig. 1 (b).

Building up the film on silicon by spin-on deposition of ten layers (A) reveals a weak PL emission with maxima at 2.28 and 2.54 eV. By comparison, the PL intensity is significantly greater in a sample containing only one layer of xerogel deposited on porous alumina (B). It is significantly increased in the case of an identical porous alumina structure containing ten spin-on layers (C), and bands are now observed with maxima at 2.54, 2.28, 2.12 and 1.99 eV. These bands are attributed to the $^5D_3 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions in Tb^{3+} ions, respectively. Terbium luminescence also increases with an increase of its concentration in the xerogel and the thickness of the porous alumina film [7].

Cooling of the samples to 4.2 – 6 K give about 5-15 - fold increase of Er and Tb PL intensity from xerogels processed on porous anodic alumina, and narrowing of the spectral lines (see Fig. 2 (b) for example). The full width at half maximum (FWHM) of the Tb-related bands in TiO_2 xerogels doped with 1.1, 2.1 and 7 at. % Tb measured at 4.2 K with a spectral resolution 0.1 nm was found to be 1.5 nm. Sequential deposition of Er-doped TiO_2 xerogel films onto anodic alumina results in one order of magnitude enhancement of the PL emission at 1.53 μm and about 2-fold narrowing of FWHM (Fig. 3) (after Ref. [8]). Cooling the samples from 300 to 4.2 K gives enhancement of the intensity of Er-related band at 1.53 μm and narrowing of FWHM from 20 to 10 nm.

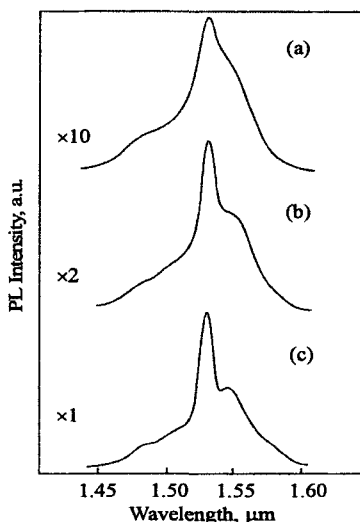


Figure 3. Room temperature PL spectra of erbium doped titania xerogel deposited onto porous anodic alumina one (a), five (b) and ten (c) times. Annealing temperature is 1173 K (after [8]).

SIMS, RBS and TEM- analyses reveal that the xerogel doped with the lanthanides develops on the walls of the alumina cells, and extends to depths of several microns after the first spin-on deposition. According to RBS and SIMS analyses of Tb and Er doped titania xerogels, mesopores of anodic alumina are filled by the xerogel after sequential spinning of ten layers (Fig. 2(c)) [7,8]. Tb PL from the xerogels processed on porous anodic alumina is green and visible by the naked eye.

Obviously, the lanthanide PL observed from the xerogels confined in porous alumina could be enhanced further by fitting the porous alumina and xerogel parameters. In such a structure the concentration of lanthanides in each layer is determined by its concentration in the sol, whereas the total number of optically active ions increases with filling of the pores. Thus, concentration quenching of lanthanide PL, as for example in Er-implanted materials, and also the precipitation of lanthanides, observed in highly doped glasses, are avoided.

4 Conclusion

The real mechanism, driving the enhancement of lanthanides PL from the structure microporous xerogel/mesoporous anodic alumina is not yet understood. It seems that in comparison with semiconductors or other non-porous materials the fabricated periodical microporous/mesoporous structure could produce less electron-phonon interaction, thus leading to lower temperature quenching. The observed enhancement of PL could be also a result of a strain, like in the case of Stranski-Karastanov and Volmer-Weber growth of low-dimensional structures, that was proposed by B. Hamilton et al [7]. Also, as was emphasized by S. V. Gaponenko and G. E. Malashkevich, the fabricated periodical structures could exhibit photonic band gap effect, revealing enhancement of emission at certain directions and its inhibition in other directions. Moreover, an increase the effective geometric thickness due to the multiply scattering of exciting wavelength in a porous medium may produce the effect of efficient absorption of the exciting light.

Further work towards enhancement of lanthanide emission from the structure microporous xerogel/mesoporous alumina and evaluation the mechanism of enhancement the PL is in progress.

5 Acknowledgements

Helpful discussions with G. E. Thompson, B. Hamilton, J. C. Pivin, V. E. Borisenko, and S. V. Gaponenko are acknowledged along with the technical help of O. V. Sergeev and I. S. Molchan. This work has been supported by the grant INTAS-Belarus 97-0250.

References

1. Hench L. L., West J. K., *Chem. Rev.* **90** (1990) 33.
2. Borisenko V. E., Hesketh P. J., *Rapid Thermal Processing Semiconductors* (Plenum Press, New-York 1997) 358.
3. Dorofeev A. M., Gaponenko N. V., Bondarenko V. P., Bachilo E. E., Kazuchits N. M., Leshok A. A., Troyanova G. N., Vorozov N. N., Borisenko V. E., Gnaser H., Bock W., Becker P., Oechsner H., *J. Appl. Phys.* **77** (1995) 2679.
4. Gaponenko N. V., Parkun V. M., Bachilo E. E., Malashkevich G. E., Borisenko V. E. In *Physics, Chemistry and Application of Nanostructures*, ed. by Borisenko V. E., Filonov A. B., Gaponenko S. V., Gurin V. S. (Minsk, 1995) 80.
5. Gaponenko N. V., Parkun V. M., Katernoga O. S., Borisenko V. E., Mudryi A. V., Stepanova E. A., Rat'ko A. I., Cavanagh M., O'Kelly B., McGilp J. F., *Thin Solid Films* **297** (1997) 202.
6. Gaponenko N. V., Mudryi A. V., Stepanova E. A., Rat'ko A. I., Sergeev O. V., Borisenko V. E., *Inorganic Materials* **34** (1998) 795.
7. Gaponenko N. V., Davidson J. A., Hamilton B., Skeldon P., Thompson G. E., Zhou X., *Appl. Phys. Lett.* **76** (2000) 1006.
8. Gaponenko N. V., Sergeev O. V., Stepanova E. A., Parkun V. M., Mudryi A. V., Gnaser H., Misiewicz J., Heiderhoff R., Balk L. J., Thompson G. E., Optical and structural characterisation of erbium-doped TiO₂ xerogel films processed on porous anodic alumina, *J. Electrochem. Soc.* (2001) – in press.
9. Kapitonov A. M., Gaponenko N. V., Bogomolov V. N., Prokofiev A. V., Samoilovich S. M., Gaponenko S. V., *Phys. Stat. Sol. (a)* **165** (1998) 119.
10. Henley W., Koshka Y., Lagowski J., *J. Appl. Phys.* **87** (2000) 7848.
11. Stepikhova M., Palmetshofer L., Jantsch W., von Bardeleben H. J., Gaponenko N. V., *Appl. Phys. Lett.*, **74** (1999) 537.
12. Thompson G. E., Wood G. C., *Nature* **290** (1981) 231.
13. Thompson G. E., *Thin Solid Films* **297** (1997) 192.
14. Gaponenko N. V., Mudryi A. V., Sergeev O. V., Borisenko V. E., Stepanova E. A., Baran A. S., Rat'ko A. I., Pivin J. C., McGilp J. F. *Spectrochimica Acta A* **54** (1998) 2177.

TECHNOLOGY OF PILLAR MICROSTRUCTURE FORMATION WITH ANODIC OXIDES

A. I. VOROBYOVA, E. A. OUTKINA

*Belarussian State University of Informatics and Radioelectronics
6 P. Browka Street, Minsk 220013, Belarus*

E-mail: vasokol@gw.bsuir.unibel.by

The technology of pillar microstructure formation based on anodic oxides of aluminum and tantalum by the multistep electrochemical method is developed. The method allowed to produce a nanometer size thin-film active elements of a three-electrode type. The main features of the developed technology and main geometrical sizes of structured layers are presented.

1 Introduction

An increase of integration level of microelectronics and creation of new devices (single-electron transistors, multi-tip cathodes, etc.) based on the quantum-size effects stimulate investigations in the field of submicrometer-, nanometer-scale self-assembled systems of quantum dots. Active area for practical applications require a new technique of nanometer array pattern formation on large-area samples and investigation of mechanisms of quantum periodic structure formation and operation.

In this paper, we describe the main features of the pillar microstructure formation by means of multi step anodization of Al/Ta film sandwiches on ceramic and silicon (100) substrates. The main characteristics of these structures, obtained by scanning electron microscopy (SEM) and chrono-voltamperometry (CVAM) techniques are presented. Information on geometrical parameters of the pillar microstructure elements has been obtained. The maximum depth/diameter ratio ("aspect ratio") for the compositions studied was 17.0 and the maximum pillar height was 540 nm (when the minimum pillar radius was 15 nm). It is not feasible to create the microelements with such parameters by any other method known.

2 Methodology

Table 1 shows the main parameters of the pillared microstructures based on anodic oxide films (AOF) obtained under different regimes.

To improve these parameters new methods of multi-step electrochemical processing of Al thin-films have been developed [1,2]. SEM was used to investigate

Table 1. Geometrical dimensions of pillared microstructures.

Electrolyte		10 % aqueous solution of sulfuric acid	3.6 % aqueous solution of oxalic acid	4 % aqueous solution of orthophospho- ric acid
Parameter	Designation	Al(500 nm)/ Ta(200 nm)/ Si(100) substrate	Al(500 nm)/ Ta(200 nm)/ Si(100) substrate	Al(500 nm)/ Ta(200 nm)/ Si(100) substrate
Anodization voltage	V_a , V	12	40	80
Anodization current density	j_a , $\mu\text{A}/\text{cm}^2$	6.0	3.0	2.0
Number of pillars	$N \times 10^8$, cm^{-2}	790(surface)	253(surface)	33(surface)
Pillar diameter	d_p , nm	30 $\pm$ 5	60 $\pm$ 5	120 $\pm$ 5
Maximum aspect ratio	β_m	17	10	4,5

the kinetics of structured layer formation. This method allowed a step-by-step monitoring of the pillar formation: sizes, density and uniformity of arrangement. As a result, it was possible to improve the technology of structured layer formation with the purpose of a specific application.

It has been established that the best results can be obtained by two-step anodization with intermediate selective chemical etching of Al_2O_3 and during prolonged electrochemical polishing of porous oxide in the anodization electrolyte under constant or decreasing voltage. In the first case, prior to the main step anodization, the formation of porous aluminum anodic oxide film on 2/3 of Al film thickness was performed under the condition of electrolyte temperature stabilization during agitation or its circulation. The main anodization of the remaining 1/3 of Al film thickness was finished without agitation of the electrolyte on rigidly fixed samples. The better rigidity of the anodizing surface, the higher regularity and uniformity of the structures obtained.

The second method is based on the extension of the anodization time (first step of the process). It improves the regularity of a pore configuration in the layer. The through porous anodization of Al film down to Ta film is followed by prolonged electrochemical dissolution (polishing of the oxide) in the same electrolyte. The thicker the aluminum film, the more prolonged anodization occurs, and its structure appears to be more regular.

3 Discussion

The effect of structure ordering is probably caused by the occurrence of artificial anisotropy (AA) in polycrystalline Al and Ta films during anodization. AA of some properties in these films is revealed under elastic tensions, electrical and magnetic fields, thermal influence, etc. Thus, with prolonged anodization the AOF are formed with large internal tensions which in conjunction with a high electric field ($E > 10^7$ V/cm) cause the ordering of polycrystalline Al and Ta films, from which the oxides are formed.

The SEM micrographs (MG) of the surface of the pillared structures after the porous AOF removal (Fig. 1(a,b)) show the influence of the polishing effect (the first process) and artificial texturing of the aluminium film surface (the second process).

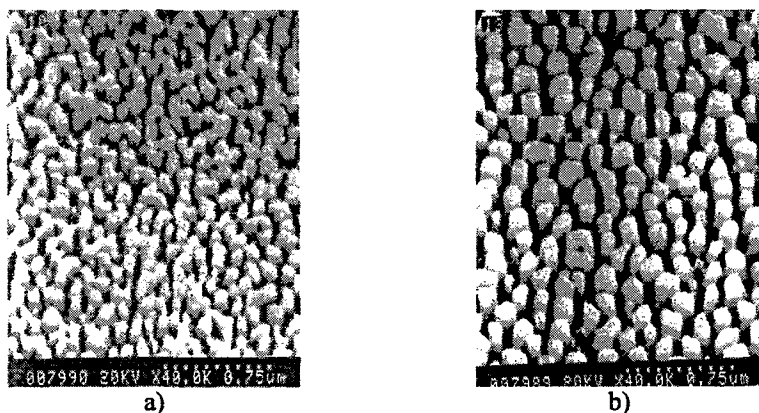


Figure 1. SEM tilt view of the surface of structured layers before (a) and after (b) polishing.

We have found optimum conditions for the regular pillar large-area structured layer formation. A new technique of local patterning of pillared layers has been developed, which may be used to fabricate a pillared matrix with a gate for thin film current controlling and other devices.

In Fig. 2, the SEM MG of pillars in the holes of the grid before metal cladding are shown. The technological process leads to the formation of a driving grid from any conductive material with the minimum hole pitch of 150 nm and a dielectric layer with quantum-size pillar-shaped conducting channels of the minimum diameter ~ 30 nm and packing density of about 10^8 - 9×10^{10} cm $^{-2}$. Such design allows to achieve the high gain efficiency and reliability. Besides, the use of AOF as a dielectric created by the simple electrochemical technique would simplify processing and reduce their production cost.

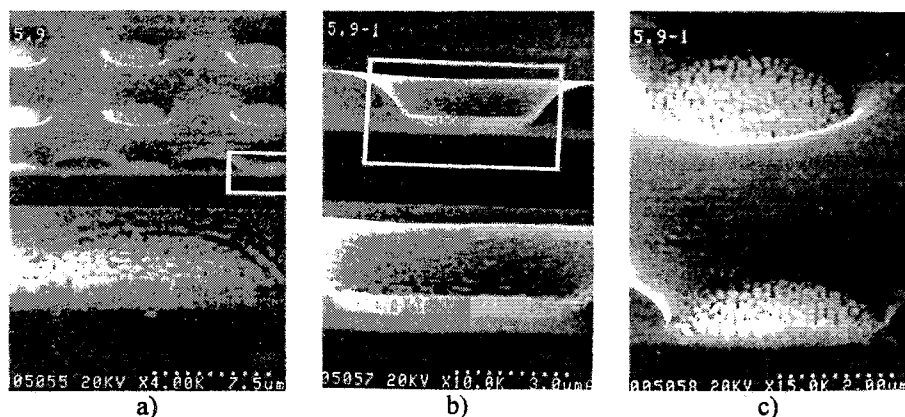


Figure 2. SEM micrographs of the surface: normal view (a), cross-section view (b), tilt view (c) of the pillars in the holes of the grid before metal cladding.

In conclusion, the technology described above allows to fabricate high performance electron devices due to formation of the control grid with an extremely low submicrometer period and to increase the number of pillar-shaped conductive channels up to 10^8 - 10^{11} cm $^{-2}$. Such large number of conductive channels, as well as a driving grid with submicrometer period is practically impossible to be created by any known masking technique.

The pillared layers arranged in the form of a matrix can be used for light-emitting structures, thin film three-electrode active devices, solar cells, functional screens and polarization elements for optoelectronics.

References

1. Vorobyova A. I., Outkina E. A., Study of pillar microstructure formation with anodic oxides, *Thin Solid Films* **324** (1998) pp.1-10.
2. Sokol V. A., Vorobyova A. I., Outkina E. A., SEM investigation of pillared microstructures formed by electrochemical anodization, *Appl. Phys. A* **67** (1998) pp. 487-492.

NEW MATERIALS AND NANOSTRUCTURES FOR ORGANIC ELECTROLUMINESCENT DEVICES

A. V. KUKHTA, E. E. KOLESNIK

*Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus
F. Skaryna ave. 70, 220072 Minsk, Belarus*

E-mail: kukhta@imaph.bas-net.by

New stable electroluminescent nanosize materials on the basis of amorphous triazinstyrene and naphthalimide derivatives, luminescing polynaphthalimide, sol-gel prepared organic-inorganic porous polysilane doped with organic Eu(III) complex, and porous alumina with organic phosphor are presented.

1 Introduction

Electroluminescent studies of organic substances were earlier held in the gas phase [1]. Electroluminescence of solid organic compound (it was anthracene crystal), placed between two electrodes, was observed for the first time in 1963 [2]. Then the researches on electroluminescence of complex organic compounds in solutions appeared [3]. But the real progress was achieved in 1987 using a multilayered nanodimensional solid organic structures [4]. The commercial issue of organic electroluminescence devices has recently (1997) started in Japan (Pioneer).

Many researchers are interested in the development of new materials and structures in order to reach new possibilities of these devices. The main problems of organics based structures are connected with their efficiency and durability. The best efficiency of some percent (about 4 %) is reached up to date, the best durability can reach more than one hundred thousand hours. In this paper new stable electroluminescent nanosize materials and structures are presented.

2 Stable electroluminescent structures

2.1 Porous alumina based structure

We proposed a new organic electroluminescent cell using porous alumina which was presented in Fig. 1 [5,6]. Organic molecules (naphthalimide derivative) are at the walls of cylindrical pores after evaporation of solvent. Luminophor molecules can be adsorbed physically or chemically depending on molecular structure. Using special compounds, the both parts of electroluminescent cell are densely connected. Molecular concentration in porous matrix can be very high without essential luminescence quenching, because adsorbing surface inside the pore is high. It is

easily to show that this value is approximately $2(h+r)/r$ more than plane surface (here h and r is the height and radius of pore, correspondingly). For pores with diameter of 100 nm it equals 6 at $h=100$ nm and 200 at $h=500$ nm.

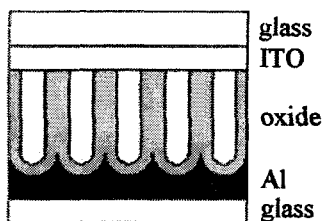


Figure 1. The structure of organic electroluminescent cell.

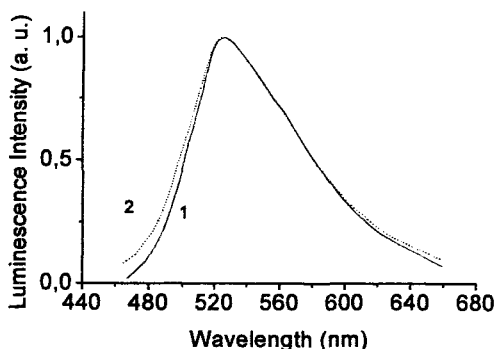


Figure 2. Photo- (1) and electro-luminescence (2) spectra of naphthalimide in porous alumina.

Moreover, the luminophor molecules can be chemically adsorbed on pore walls and formed a monomolecular layer resulting in the luminescence quenching decrease.

We observed the intensive electroluminescence of 4-methyl-amino-N-(o-tolyl)-1,8-naphthalimide in proposed structure. The required applied voltage is considerably higher than in usual electroluminescent devices. But the thickness of this structure is too high. For 300 nm oxide thickness the threshold potential is 27 V. The main problem now is to find an optimal thickness alumina layer between the aluminium and pore space. The electroluminescence spectrum almost fully coincides with photoluminescence one, as presented in Fig. 2. A slight difference is apparently connected with additional radiation of excited particles of alumina layer. Any luminophor or their mixture can be easily introduced into this matrix.

2.2 *Eu-complex doped sol-gel prepared organic-inorganic polysilane*

We developed a new electroluminescent material on the basis of nanoporous organic-inorganic polysilane containing new effective Eu(III) complex [7]. This polymer prepared by sol-gel method is known as high thermally stable. The obtained thin films are very homogeneous and transparent with working temperature over 250 °C. The luminescence quantum efficiency of Eu complexes in this polymer is an order of magnitude higher than in inorganic matrix due to the absence of free hydroxyl groups being luminescence quenchers. The Eu(III)

complex consist of $\text{Eu}(\text{Br-BTFA})_3 \cdot \text{TPPO}$ (where HBr-BTFA – bromine-benzoyltrifluoroacetone and TPPO is triphenylphosphin oxide). The process of a film preparation includes the hydrolysis of vinyltriethoxysilane in aqueous-alcohol solution and the following dissolution of Eu(III) complex. The prepared sol can be deposited on the various substrates by spin-coating method. The annealing temperature of the films is 140°C for 5 min. In the case of organic-inorganic polymer the forming medium is nearly neutral and polymeric molecules form pores, in which Eu -complex molecules are encapsulated.

A simple electroluminescent cell consists of a glass plate coated with ITO layer as a positive electrode, 60 nm Eu -activated above mentioned polymer, and vacuum deposited aluminium layer as a negative electrode. The active area was $4 \times 4 \text{ mm}^2$. It can be noted that this matrix is transparent in a wide spectral region from about 218 nm through the near IR. Intensive electroluminescence was observed after voltage applying. The most intensive is narrow peak near 615 nm. It changes more than three orders of magnitude from the threshold to 23 V. The electroluminescence intensity does not essentially change up to 250°C .

2.3 *Polynaphthalimide based electroluminescent structure*

Very promising polymers for this purpose are polyimides. They have a very high chemical, thermal (until about 400°C), and radiation stability, and high dielectric and mechanical properties. As a rule, polyimides are donor-acceptor macromolecules being efficient electron and hole conductors. Due to blue absorption they can radiate in green and red spectral regions. The problem is to enhance the luminescence efficiency of these polymers. We try to use naphthalimide derivatives for construction of new luminescent polyimide molecules. We synthesised a new polymer using luminescent N,4-derivative of 1,8-naphthalimide and diamine [8]. The obtained polymer fluoresces intensively in a green and yellow spectral region in solution (polyamide acid) and thin film. We created a simple electroluminescent cell consisting of ITO layer as a positive electrode, 120 nm polynaphthalimide, and aluminium vacuum deposited layer as a negative electrode. The active area was $4 \times 4 \text{ mm}^2$. Its electroluminescence spectrum slightly differs from photoluminescence one in the shortwave region. This difference is possibly connected with radiation of diimide part of molecule. Electroluminescence intensity was not practically changed after heating of the electroluminescent cell to 220°C in a special oven.

2.4 *Amorphous triazinstylbene based electroluminescent cell*

Triazinstylbene molecules have unique properties. Its chemical structure having some branched aminogroups is similar to the structure of triphenyldiamine being a well known hole transporting substance. It was found that naphthalimide and partly some triazinstylbene derivatives form excellent stable smooth glasslike thin films

without pinholes. The molecules in thin solid films are in monomolecular state, their absorption and fluorescence spectra are slightly shifted relatively the solution spectra. Their fluorescence lifetimes in both states (solution and amorphous film) are close to each other. The fluorescence quantum yield under excitation into the long wave and short wave absorption bands are approximately equal. Moreover, the spectrum of triazinstylbene-OD fluorescence overlaps the spectrum of naphthalimide absorption and result in effective energy transfer.

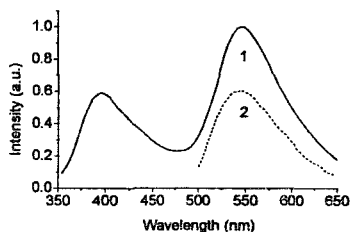


Figure 3. Electroluminescence spectra of naphthalimide with triazinstylbene (1) and TPD (2).

In a two layered cell, the intensive both triazinstylbene-OD (60 nm) and 4-methyl-amino-N-(o-tolyl)-1,8-naphthalimide (60 nm) [9] electroluminescence was observed. The electroluminescence spectrum completely coincides with a photoluminescence spectrum and it is much wider and more intensive than in the naphthalimide-triphenyldiamine cell at the same conditions (Fig. 3). It means that triazinstylbene film can also radiate and transfer holes more effectively than TPD.

3 Conclusion

Very stable light emitting nanosize materials and structures for practical usage can be obtained with amorphous triazinstylbene and naphthalimide derivatives, luminescing polynaphthalimide, sol-gel prepared organic-inorganic polysilane doped with organic Eu(III) complex, and porous alumina with organic phosphors.

References

1. Ambrush I., Radiation spectra of organic compounds in gas discharges, *Uspekhi Khimii* **26** (1957) pp. 345-361 (in Russian).
2. Pope M., Kallmann H., Magnante P. J., Electroluminescence in organic crystals, *J. Chem. Phys.* **38** (1963) pp. 2042-2043.
3. Hercules D. M., Chemiluminescence resulting from electrochemically generated species, *Science* **145** (1964) pp. 808-809.

4. Tang C. W., VanSlyke S. A., Organic electroluminescent diodes, *Appl. Phys. Lett.* **51** (1987) pp. 913-915.
5. Kukhta A. V., Kolesnik E. E., Shakah G. H., Taoubi M. I., Mozalev A. M., Smirnov A. G., New organic electroluminescence structures using porous alumina films, *Proc. SID* **31** (2000) pp. 645-647.
6. Kukhta A. V., Kolesnik E. E., Shakah G. H., Taoubi M. I., Mozalev A. M., Porous alumina based cathode for organic light-emitting devices, *Proc. SPIE* **4105** (2000) pp. 405-412.
7. Kukhta A. V., Kolesnik E. E., Pavich T. A., Taoubi M. I., A new stable and effective organic phosphor: Eu-complex doped organic-inorganic polymer prepared by sol-gel method, in *Display Researches: Proc. Int. Conf.* (Palm Beach, 2000) pp. 155-158.
8. Kukhta A. V., Kolesnik E. E., Taoubi M. I., Drozdova D., Prokopchuk N. R., Polynaphthalimide is a new polymer for organic electroluminescence devices, *Synth. Met.* (in press).
9. Kukhta A. V., Kolesnik E. E., Taoubi M. I., et al., Electroluminescence of belophores in a wide spectral region, *J. Appl. Spectrosc.* **67** (2000) pp. 678-680.

CADMIUM SELENIDE NANOCRYSTALS INSIDE PLASTIC MICROSPHERES: A QUANTUM DOT IN A PHOTONIC DOT STRUCTURE WITH UNUSUAL OPTICAL PROPERTIES

M. V. ARTEMYEV

*Institute for Physico-Chemical Problems of Belarussian State University
Leningradskaya str. 14, 220080 Minsk, Belarus*

E-mail: m_artemyev@bigfoot.com

A number of experimental data is presented which demonstrate the realization of the conception of quantum dot-in-photon dot structure. Chemically synthesized CdSe nanocrystals are incorporated into both monolithic and hollow polymethylmethacrylate micron-sized microspheres. The emitting properties of nanocrystals are strongly modified inside microspheres resulting in a number of sharp discrete modes. The effective coupling of broad nanocrystal emission with quantized photon states in spherical microcavity brings the ability to create room temperature nearly thresholdless microlasers with optical pumping.

1 Introduction

II-VI semiconductor nanocrystals, like CdSe synthesized via high temperature colloidal chemistry routes are useful objects to study optical properties of quantum dots [1,2]. Being modified by special methods, e.g. additional surface epitaxial layers of wide gap semiconductors (ZnS, CdS) these nanocrystals exhibit bright stable photoluminescence at room temperature which makes them attractive for various applications, like fluorescence biological labels etc. [3,4].

Generally, photoluminescence spectra of ensemble of CdSe nanocrystals consist of a single lorentzian-shape band broadened due to certain size distribution over the ensemble. This band undergoes the spectral shift to the blue with decreasing size of nanocrystals (the well-known size quantization effect [1]). The nanocrystals under size quantization conditions often called quantum dots (QDs). The broad photoluminescence band can be strongly modulated when nanocrystals are incorporated in optical microcavity [5]. Recently, it has been proposed that among others the high quality polymeric micron-sized spheres can serve as three-dimensional (3D) optical microcavities for emitters incorporated inside, or attached to the surface [6,7]. Polymeric microspheres allow to concentrate the light emitting from nanocrystals to only few discrete optical modes which is essential step toward creation of room temperature microlasers with optical pumping.

In this paper the preparation methods for polymeric microspheres doped with (CdSe)ZnS QDs are described and photoluminescence properties of new quantum dot-in-photon dot structure are discussed.

2 Experimental

Highly luminescent CdSe QDs covered with ZnS epilayers were synthesized by high temperature reaction of organometallic precursors in strongly coordinating solvent trioctylphosphine oxide (TOPO) [8]. The diameter of CdSe core is about 4 nm and thickness of ZnS shell of only few monolayers. (CdSe)ZnS QDs were dissolved in methylmethacrylate (MMA), a precursor for well-known organic glass polymethylmethacrylate (PMMA). A part of MMA solution containing a small amount of dissolved PMMA was dropped to water under vigorous stirring to which hexadecyltrimethylammonium bromide (HDAB) was added as emulsion stabilizer. Since, MMA is not miscible with water it creates an emulsion of small (few hundred microns) liquid microdroplets containing (CdSe)ZnS QDs. Next, the vessel with microemulsion keeps open at 60-80 °C under vigorous stirring for 2-4 h till most part of MMA evaporates out of emulsion. On this stage a PMMA remaining in each liquid microdroplet creates a solid microsphere, either monolithic, or hollow depending on the concentration of reagents (MMA, PMMA, HDAB), temperature of emulsion and stirring speed. QDs are distributed randomly over PMMA microsphere. In case of hollow one the most part of QDs is collected in thin PMMA shell leaving hollow core almost empty. Further the microspheres were centrifugated out of mother solution and placed on the surface of quartz glass. A quartz sample with microspheres was mounted on the holder.

The photoluminescence was excited by cw Ar-ion laser ($\lambda = 488$ nm, 50 mW). The emitted light was collected by a microscope objective with high spatial resolution and passed through double monochromator equipped with cryogenically cooled CCD camera. Simultaneously, the optical image of microspheres can be registered with additional video camera.

3 Results and discussion

Fig. 1a represents an image of various PMMA microspheres doped with (CdSe)ZnS QDs. Among monolithic microspheres which are seen as homogeneous spots there is a number of hollow spheres with thin PMMA shell and empty core.

In the bottom right part of the image even a cut hollow half-microsphere can be found. The photoluminescence images of hollow and monolithic microspheres also are different. In Fig. 1b for hollow microsphere two rims, outer and inner are seen clearly. A possible mechanism of hollow sphere formation together with monolithic ones in the same solution is as follows. Slow evaporation of MMA out of each microdroplet in the emulsion results in increasing concentration of PMMA and slow homogeneous compression of microdroplets. This process gives finally solid PMMA core and monolithic microsphere. At high initial concentration of PMMA and high

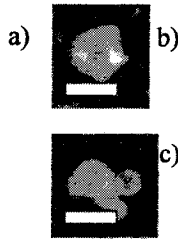
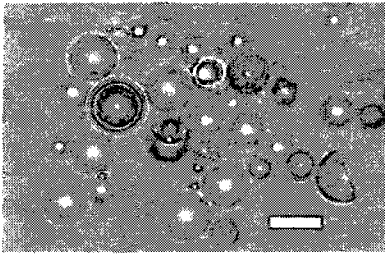


Figure 1. a) Visible image of PMMA microspheres doped with (CdSe)ZnS QDs. b) Photoluminescence image of hollow microsphere doped with (CdSe)ZnS QDs. c) Photoluminescence image of monolithic microspheres doped with (CdSe)ZnS QDs. Bar is 10 μm .

evaporation rate rather a solid PMMA shell could be formed in each microdroplet since, even very thin solid PMMA surface skin prevents from compression of microdroplets. In this case remaining MMA diffuses through PMMA skin leaving empty core. Possible impacts and coalescence between microdroplets in the emulsion destroy this process resulting in relatively small amount of hollow microspheres in final mixture as compared to monolithic or nonspherical and broken ones.

When the emitting dipole, for example CdSe QD, is placed inside a spherical microcavity the light is travelling over the microsphere rim due to total internal reflection at microsphere interface. The most important consequence of this effect is those optical modes can only exist inside spherical microcavity with optical pathway being divisible to corresponding wavelength. These modes are called whispering gallery modes (WGM) [9]. In other words, there is a discrete number of allowed photon states inside spherical microcavity and by analogy with quantum dots such microsphere can be treated as photonic dot (PD).

Fig. 2 demonstrates how incorporation of QDs into PMMA PDs affects on their

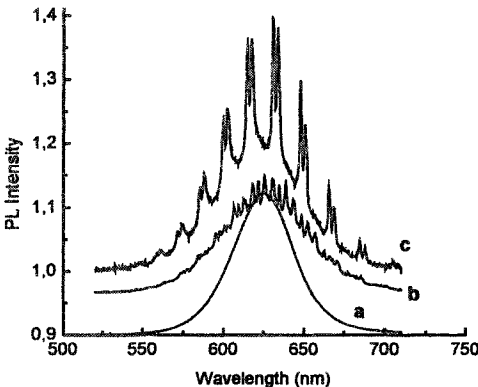


Figure 2. Room temperature photoluminescence spectra of (CdSe)ZnS QDs (a), monolithic (b) and hollow (c) PMMA PDs doped with (CdSe)ZnS QDs.

photoluminescence spectra. Initial broad band from QDs alone (curve a) is modulated by a number of sharp modes in case of monolithic PMMA PD. Still, most part of spectrum remains unmodulated due to QDs located far from the surface of PD with minimum coupling of light to WGMs. In case of hollow PD (curve c) nearly all QDs are placed in thin surface PMMA shell with strong light coupling. As

a result, strong discrete sharp lines appear in photoluminescence spectrum with much weaker background. Hence, using hollow PMMA microspheres as photonic dots doped with CdSe QDs the emitting light can be effectively concentrated to only few very sharp modes which opens the way for effective room temperature lasing from chemically synthesized II-VI quantum dots [10].

4 Acknowledgements

I thank Prof. U. Woggon for helpful discussion. This work was supported in part by grant INTAS-Belarus 97-0250.

References

1. Woggon U., *Optical properties of semiconductor quantum dots* (Springer-Verlag Berlin Heidelberg, 1997).
2. Gaponenko S. V., *Optical properties of semiconductor nanocrystals* (Cambridge University Press, Cambridge, 1998).
3. Bruchez M. Jr., Moronne M., Gin P., Weiss S., Alivisatos A. P., Semiconductor nanocrystals as fluorescent biological labels, *Science* **281** (1998) pp. 2013-2016.
4. Chan W. C. W., Nie S., Quantum dot bioconjugates for ultrasensitive nonisotropic detection, *Science* **281** (1998) pp.2016-2018.
5. Gaponenko S. V., Kapitonov A. M., Gurinovich L. I., Bogomolov V. N., Artemyev M. V., Rogach A. L., Eychmüller A., Electrons and photons in mesoscopic structures: quantum dots in a photonic crystals and in a microcavity, *Proc. SPIE*, **3734** (1999) pp. 369-372.
6. Artemyev M. V., Woggon U., Quantum dots in photonic dots, *Appl. Phys. Lett.* **76** (2000) pp. 1353-1355.
7. Artemyev M. V., Woggon U., Wannemacher R., Photons confined in hollow microspheres, *Appl. Phys. Lett.*, in press (2001).
8. Hines M. A., Guyot-Sionnest P., Synthesis and characterization of strongly luminescing ZnS-capped CdSe nanocrystals, *J. Phys. Chem.* **100** (1996) pp. 468-471.
9. *Optical Processes in Microcavities*, ed. by Chang R. K., Chamillo A. J., Advanced Series in Applied Physics 3 (World Scientific, Singapore, 1996).
10. Pelton M., Yamamoto Y., Ultralow threshold laser using a single quantum dot and a microsphere cavity, *Phys. Rev. A* **59** (1999) pp. 2418-2421.

POROUS SILICON AS A MATERIAL FOR ENHANCEMENT OF ELECTRON FIELD EMISSION

A. A. EVTUKH, V. G. LITOVCHENKO, YU. M. LITVIN, A. A. EFREMOV
YU. V. RASSAMAKIN, A. V. SARIKOV, D. V. FEDIN

*Institute of Semiconductors Physics
45 Prospekt Nauki, 03028 Kiev, Ukraine*

E-mail: evt@book.semicond.kiev.ua

The influence of a porous layer on silicon tips upon the electron field emission has been investigated. The porous silicon layer obtained by electrochemical method and stain-etching was studied. The improvement of emission parameters in comparison with those for single-crystalline Si tips (without porous layer) was observed at some growth conditions. At lower emission current densities the non-monotonous current-voltage characteristics were revealed. The effect of the porous silicon layer upon the electron field emission was explained by the formation of asperities (fibres) on the silicon surface. The formation of porous silicon is simulated with the of single-pore approach.

1 Introduction

The porous silicon (PS) is an attractive material for application in electron field emission devices. The apex of the cathode from which electrons are emitted is the critical unit of any vacuum microelectronic device. For low voltage applications its radius should be very small leading to the large field enhancement coefficient. A fabrication of very sharp uniform emitters is difficult. One approach includes covering the cathodes with a thin layer of material with low work function, so that electron field emission is obtained at the lower voltages [1-4]. Growing PS layers on silicon tips is an approach for the formation of natural sharp asperities instead of single sharp emitting point creation at the apex of each cathode. Under these conditions the emission is controlled by the asperities rather than a single "macroscopic" apex of the emitter. PS layers provide nanometer-size fibrils (wires) on the silicon tip surface and can increase the electrical field enhancement coefficient and emission areas. Hence, they can improve emission characteristics [5-8].

In the present work we study the influence of PS layers formed on silicon tips upon electron field emission. Our results show the perspective of PS layer application in vacuum microelectronic devices to improve electron field emission.

2 Experiment

2.1 Formation of silicon tips

Arrays of silicon emitter tips were fabricated by wet chemical etching using lithography process with formation of silicon points [9]. The cathodes were etched on (100) Si n-type wafers ($N_d=10^{15} \text{ cm}^{-3}$) with using Si_3N_4 film as a masking layer. The tip sharpening was performed by oxidation of the as-etched tips at 900°C in wet oxygen. The oxide was removed in $\text{HF}:\text{H}_2\text{O}$ solution. This sharpening technique allows to produce tips with a curvature radius of 10-20 nm. The arrays have been fabricated on the area of $8 \times 8 \text{ cm}^2$ the tip density $2.5 \times 10^5 \text{ cm}^{-2}$.

2.2 Formation of porous silicon layers

PS layers were formed by electrochemical and stain-etching of silicon. In the case of electrochemical etching the PS layers were formed on silicon tips by anodization in 48 % HF ethanol solution under the illumination with intensity 30 mW/cm^2 . The thickness of PS layers and, consequently, height of silicon fibrils formed increase with time of anodic etching [10]. Also the size of pores and, consequently, the degree of porosity, increase and fibril thickness decreases with the growth of anodization current [10]. Under the stain-etching the samples were immersed into the solution ($\text{HF}:\text{HNO}_3:\text{H}_2\text{O}=1:3:5$ with 49 % HF and 70 % HNO_3). The etching was performed under illumination for up to 10 min and PS layers less than $1 \mu\text{m}$ thick were obtained. Due to the higher resistivity of PS in comparison with single-crystalline Si we tried to obtain thin ($<1 \mu\text{m}$) PS layers to minimize current limitation.

2.3 Measurements

The emission currents from silicon tip arrays coated with thin PS layers were recorded in the vacuum system (10^{-6} Torr). The emission current was measured in the ungated cathode-anode structure. The emitter-anode spacing L was constant ($10-20 \mu\text{m}$). We fabricated a test diode structure by the sandwiching of anode and cathode plates. A silicon wafer was used as a cathode and ITO coated quartz plate or aluminium was used as anode. A teflon film spacer ($10-20 \mu\text{m}$) was used to keep the two plates separated each from other. The emission current-voltage (I-V) characteristics were obtained with current sensitivity of 5 nA in the voltage range up to 1500 V.

3 Results and discussions

Current-voltage characteristics of the electron field emission from silicon tip array obtained by the wet chemical etching with electrochemically created PS layers are

presented in Fig. 1(a, b). The emission from the tip array without PS layer is depicted for comparison. The preparation conditions of the PS layer strongly affect the emission properties.

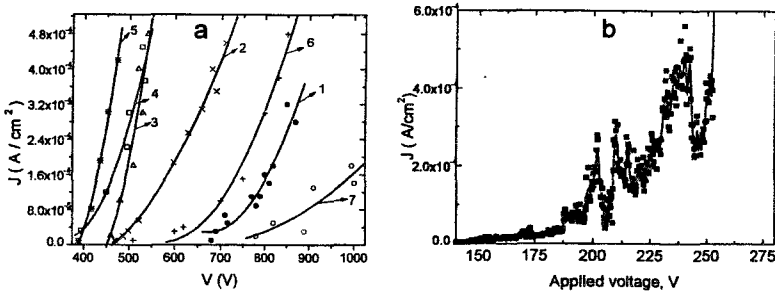


Figure 1. Current-voltage characteristics for a silicon tip array with porous silicon layer: (a) 1, Si tip array; 2-7, porous Si layer on tip; 2, $J/t=25 \text{ mA cm}^{-2} - 5 \text{ s}$; 3, $J/t=25 \text{ mA cm}^{-2} - 10 \text{ s}$; 4, $J/t=25 \text{ mA cm}^{-2} - 30 \text{ s}$; 5, $J/t=25 \text{ mA cm}^{-2} - 40 \text{ s}$; 6, $J/t=25 \text{ mA cm}^{-2} - 60 \text{ s}$; 7, $J/t=10 \text{ mA cm}^{-2} - 60 \text{ s}$ (J/t is the current density to time ratio during formation of the porous silicon layer); (b) first measurements, $J/t=25 \text{ mA cm}^{-2} - 30 \text{ s}$.

The non-monotonous behaviour of the current-voltage curves can be associated with peculiarities of the electron field emission from the PS coated silicon tip arrays. At the beginning (at the lowest voltages) the electron field emission occurs from some part of sharp fibrils on the top of the tips. But due to high local current these fibrils (asperities) are heated and blunted (destroyed) because of melting and/or due to residual gases bombardment. As a result the emission from fibrils with smaller radii of curvature can take place. The repeated and reversed measurements of the emission currents at the same point do not reproduce previous peculiarities.

To explain the features of current-voltage characteristics and to compose them for different conditions of PS layer formation we have determined the threshold voltages and the emitting area (α) of 7.5×10^3 tip arrays and local field enhancement factor (β) from the Fowler-Nordheim equation according to [1,11]. For calculation of α and β we have used electron work function $\Phi=4.15 \text{ eV}$ for n-type silicon [12].

The emission parameters V_{th} , α , β vs duration of the electrochemical etching are given in Table 1. They are determined by the thickness and porosity of PS and height of fibrils. The anodization current density defines the size of pores (number of asperities on the surface and thickness of single fibrils), and anodization time influences on the depth of pores (heights of the fibrils). The asperities density and their shape are controlled by the conditions of porous silicon layer preparation.

To understand the influence of current density and duration the electrochemical etching on PS parameters we simulated the growths of the porous layer in silicon using the single-pore approach. We considered the formation of an isolated pore in the single-crystalline silicon due to the electrochemical reaction between silicon and HF with the participation of holes in the aqueous medium. The system of evolution

Table 1. Emission parameters of tips covered by porous silicon layer.

Materials	α , cm ²	β , cm ⁻¹	V_{th} , V
Si tips	1.5×10^{-14}	1.6×10^{-5}	530
	2.9×10^{-12}	8.2×10^4	530
Porous Si tips			
5mA cm ⁻² , 120 s	6.8×10^{-10}	3.3×10^4	591
	7.2×10^{-16}	1.9×10^5	591
10mA cm ⁻² , 60 s	1.8×10^{-8}	3.5×10^4	730
25mA cm ⁻² , 5 s	9.6×10^{-12}	6.6×10^4	450
25mA cm ⁻² , 10 s	2×10^{-8}	4.7×10^4	400
25mA cm ⁻² , 30 s	1.2×10^{-11}	1.2×10^5	350
25mA cm ⁻² , 40 s	1.3×10^{-15}	2.8×10^5	390
25mA cm ⁻² , 60 s	2×10^{-8}	4.7×10^4	455

equations described the process of the pore growth was numerically solved with the detailed account of the reagent transport and by-products inside the pore. The pore length linearly increases with time at the initial etching stages Fig. 2 slows down its growth at the prolonged etching. For bigger current densities the deviation of the growth law from the linear one occurs at the shorter times. It results from the diffusion-limited supply of HF. The simulation is in qualitative agreement with experimental data [19]. Fig. 2(b) also shows the evolution of the pore radius on the front side of the wafer with the etching time at different levels of anodization current.

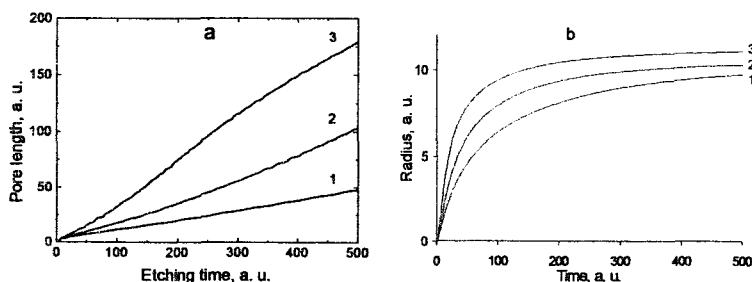


Figure 2. The dependence of the pore length (a) and its radius on the front side of the wafer (b) upon etching time. Current density (a. u.): 1 – 0.2, 2 – 0.4, 3 – 0.8.

After anodization at 30 mA/cm² during 210 s the silicon tips had a rather developed surface and were strongly blunted. The emitting areas and the local field emission enhancement factor determined by Fowler-Nordheim plots (Table 1) allow us to explain the observed results. By formation of the porous silicon layer we created asperities (nanometer-sized) on the silicon surface and, hence, increased the emitting area in comparison with silicon tips. The growth of α with ionization time ($J=25$ mA/cm²) is observed up to 30 s. The field enhancement factor β in the initial

period of time increased. With following growth the emitting area decreases and β increases with the etching time. The non-monotonous changes of α and β with time allow us to explain the emission characteristics behavior taking into account the variation of density and the height/base ratio of asperities (fibrils) on the surface. The correct determination of effective work function from silicon tip covered by the PS layer was impossible due to the uncertainty of radii and heights of emitting points.

References

1. Branston D. W., Stephani D., Field emission from metal-coated silicon tips, *IEEE Trans. Electron. Dev.* **ED-38** (1991) pp. 2329-2333.
2. Litovchenko V. G., Evtukh A. A., Marchenko R. I., Klyui N. I., Semenov V. A., The enhanced field emission from microtips covered by ultrathin layers, *J. Micromech. Microeng.* **7** (1997) pp. 1-6.
3. Litovchenko V. G., Evtukh A. A., Marchenko R. I., Klyui N. I., Semenov V. A., Enhancement of field emission from cathodes with supethin diamond-like carbon films, *Appl. Surf. Sci.* **111** (1997) pp. 213-217.
4. Silva S. R. P., Forrest R. D., Poa C. H., Klan R. U. A., Carey J. D., Burdeh A. P., Improved electron field emission properties from surface treated amorphous carbon thin films. In *Proc 12th Int. Vac. Microelectron. Conf.* (Darmstadt, Germany, 1999) p. 306.
5. Evtukh A. A., Litovchenko V. G., Marchenko R. I., Klyui N. I., Popov V. G., Semenov V. A., Peculiarities of the field emission with porous Si surfaces, covered by ultrathin DLC films, *J. Phys. IV* **6** (1996) pp. C5-119 - C5-124.
6. Wilshaw P. R., Boswell E. C., Field emission from pyramidal cathodes covered in porous silicon, *J. Vacuum Sci. Technol. B* **12** (1994) pp. 662-665.
7. Takai M., Yamashita M., Wille H., Enhanced electron emission from n-type porous Si field emitter arrays, *Appl. Phys. Lett.* **66** (1995) pp. 422-423.
8. Kleps I., Nicolaesch D., Lungu C., Musa G., Bostan C., Caccavale F., Porous silicon field emitters for display applications, *Appl. Surf. Sci.* **111** (1997) pp. 228-232.
9. Marcus R. B., Ravi T. S., Gmitter T., Chin K., Liu D., Orvis W. J., Ciarlo D. R., Hunt C. E., Trujillo J., Formation of silicon tips with < 1 nm radius, *Appl. Phys. Lett.* **56** (1990) pp. 236-238.
10. Hejjo A.I., Rifai M., Christophersen M., Ottow S., Carstensen J., Foll H., Dependence of macropore formation in n-Si on potential, temperature and doping, *J. Electrochem. Soc.* **147** (2000) pp. 627-635.
11. Brodie I., Spindt C. A., Vacuum microelectronics, *Adv. in Electron. and Electron Phys.* **83** (1992) pp. 1-106.
12. Sze S. M., *Physics of semiconductor devices* (A Wiley - Intersciences Publication John Wiley & Sons, New-York 1981).

ON USE OF BESSEL LIGHT BEAMS IN NANOTECHNOLOGIES

N. S. KAZAK, A. A. RYZHEVICH, A. N. KHILO

*Institute of Physics, NAS of Belarus
68, F. Skaryna ave., 220072 Minsk, Belarus**E-mail: tol@dragon.bas-net.by*

A method of focusing of Bessel light beams of zero and first orders is proposed for the first time and studied theoretically and experimentally. This method allows to form axially-symmetric light fields with radii of its central bright or dark spots changing linearly with axial coordinate. The minimum possible spot dimensions are on the order of a wavelength. A new optical element for production of converging Bessel beams is proposed. It is suggested to use focused Bessel beams in nanotechnologies for guiding of cold atoms.

1 Introduction

The interest to applications of controlled cold atoms in nanotechnologies is continually increasing during recent years. Atomic beams can be used in lithography, for production of microstructures, gratings, and microcircuit chips. Quantum computations can be realized using cold ions confined in a linear trap [1]. For cooling and guiding atoms, high-intensity laser beams with narrow spectral line are usually used. Besides widely used Gaussian beams, Bessel light beams can also be applied for manipulation with cold atoms [2]. The specific structural feature of a Bessel light beam is that the wave vectors k of its Fourier spectrum lies on a conical surface (Fig. 1). The transverse $q = k \sin \gamma$ and longitudinal $k_z = k \cos \gamma$ components of

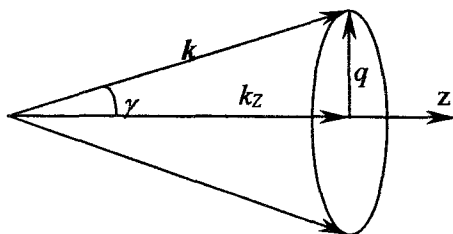


Figure 1. Spatial spectrum of the Bessel light beam.

all wavevectors are equal, where γ is a cone angle (conicity parameter) of the Bessel beam.

Zero-order Bessel light beam (BLB_0) has an intensity distribution described by the following equation: $I(\rho) \sim J_0^2(q\rho)$, where J_0 is the zero-order Bessel function, ρ is the radial coordinate. The advantage of BLB_0 over Gaussian beams is the almost

nondiverging central peak of micron size of the former, which exists in quite an extended region of the optical axis. The narrow central peak of BLB_0 allows to confine atoms with higher efficiency and transport them over longer distances. However, because the central peak radius of BLB_0 does not depend on the longitudinal coordinate, BLB_0 cannot be used for focusing of cold atoms.

Gaussian beams can be used for trapping of cold atoms in its central region, if its frequency is red-detuned. However, blue-detuned Laguerre-Gaussian light beams of first order (LG_{01}), which have a screw wavefront dislocation, can also be used [3]. Unlike Gaussian beams, the intensity of LG_{01} on the axis is zero. Cold atoms are confined in the area close to the axis, and because the intensity in this area is low, the number of excited atoms is small. It is known that there is the energy transfer from excited atoms to atoms in ground state that is the major factor that causes atoms to leave the trap. Therefore, due to the central intensity minimum, LG_{01} beams can be used for creation of more effective atom traps. Furthermore, the converging LG_{01} can be used to focus the beams of particles which are propagating inside LG_{01} .

For manipulations with atomic beams it is possible to use first-order Bessel beams (BLB_1), whose intensity distribution is described by the first-order Bessel function: $I(\rho) \sim MJ_1^2(q\rho)$. Because these beams have a screw wavefront dislocation of first order, their axial intensity is zero. The first bright ring of BLB_1 has micron dimensions, and the region in which it does not diverge has the same extent as that of the BLB_0 . Therefore, from the point of view of manipulation with atomic beams, usual BLB_1 has the advantages of both BLB_0 and LG_{01} , although together with BLB_0 , BLB_1 cannot be used for focusing of atomic beams [3].

We propose simple methods of formation of convergent Bessel beams, which can be used not only to guide, but also to focus atomic (ion) beams, which are used in nanotechnologies.

2 Production of Bessel light beams of the zeroth and the first order

One of the most effective method of formation of BLB_0 is the use of axicons (conical lenses) as it is illustrated in Fig. 2.

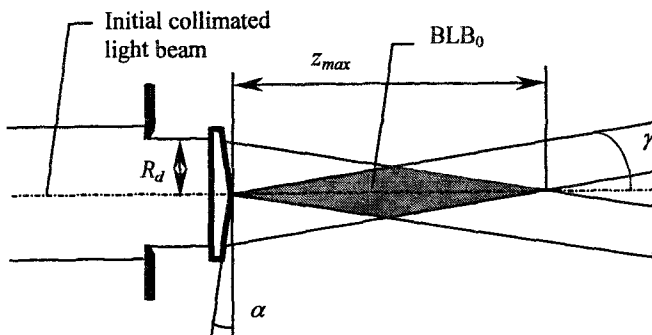


Figure 2. Production of BLB_0 by the axicon with the cone base angle of α .

The Bessel beam exists in the region which approximately corresponds to the figure formed by rotating the shaded rhomb and has finite dimensions. The

maximum distance from axicon, at which the BLB still exists, is $z_{max} = R_d/\gamma$, where R_d is the radius of the diaphragm limiting the collimated coherent light beam illuminating the axicon.

The intensity distributions in experimental BLB_0 (Fig. 3a) is described by the squared Bessel function of the 0-th order (Fig. 3b).

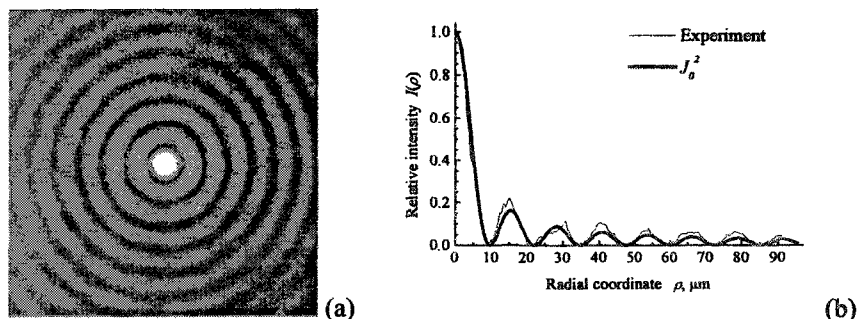


Figure 3. Experimentally obtained BLB_0 (a) and intensity distribution in the BLB_0 (b).

The most widely used method of production of BLB_1 is holographic method [4]. We developed a universal method of production of beams with screw wavefront dislocations by means of biaxial crystals [5]. It is shown in Fig. 4.

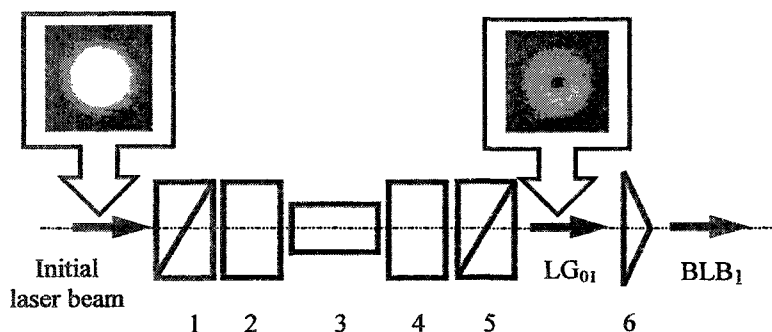


Figure 4. The scheme for production of BLB_1 : 1 - input beam with WFS D_0 ; 1, 5 - polarizers; 2, 4 - $\lambda/4$ -plate; 3 - biaxial crystal; 6 - axicon.

This method allows to transform BLB_0 directly into BLB_1 , and also to transform a Gaussian beam into LG_{01} , from which the BLB_1 is then formed with an axicon. Period of maxima and minima of BLB_1 is approximately equal to that of BLB_0 with the same conicity angle (Fig. 5).

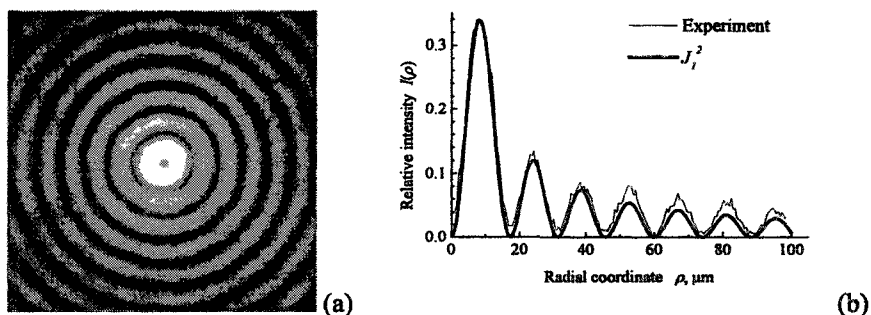


Figure 5. Experimentally obtained BLB₁ (a) and intensity distribution in the BLB₁ (b).

The forces acting upon the atoms are proportional to the gradient of light intensity. The transverse distributions of forces acting upon atoms near optical axes of BLB₀ and BLB₁ are shown in Fig. 6.

The diameter of the central bright spot of BLB₀ and the central dark spot of BLB₁ depends on the angle α at the axicon basis. The dependence of diameter of 0-th maximum d_0 on the axicon base angle α is given by $d_0 = 2.4 \lambda / \pi \sin[\alpha(n-1)]$, where λ is the wavelength of laser radiation, n is the refractive coefficient of the axicon material. This dependence is visualized in Fig. 7.

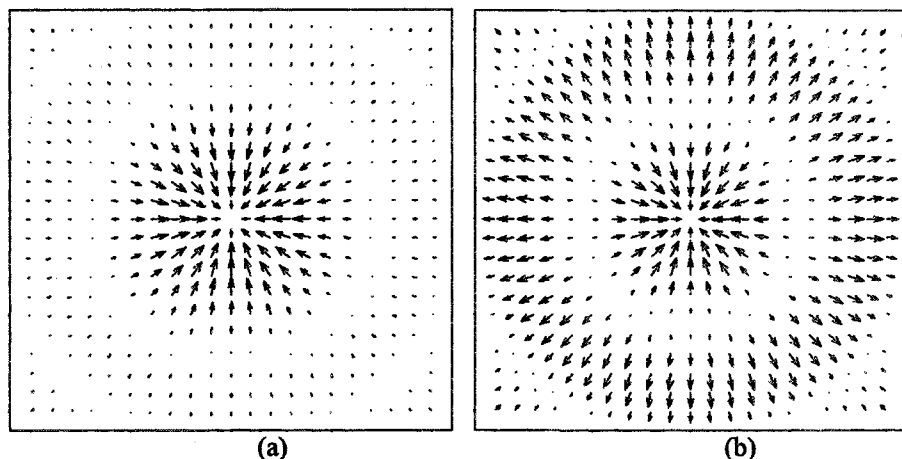


Figure 6. The transverse distributions of forces acting upon atoms near optical axes of (a) BLB₀ and (b) BLB₁ with conicity angle of 2 deg. The depicted region corresponds to 15 μm .

For technological purposes, it is sometimes desirable to have beams with central peak dimensions which are less than 1 μm . It can be inferred from Fig. 7 that axicons with α which is larger than 10 deg are required to produce Bessel beams with such small central peaks. But production of high-quality axicons with large

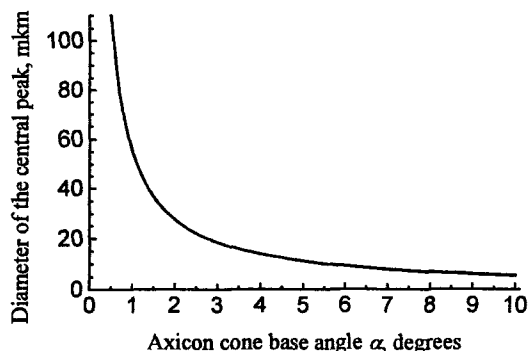


Figure 7. Diameter of the central peak versus axicon base angle.

3 Production of converging BLBs

In order to produce a converging BLB we propose to use a positive lens placed before the axicon in schemes of Figs. 2, 4. In our modeling we assumed that the lens is directly before the axicon. In this case the combination of the lens and the axicon is equivalent to an optical element which input face is spherical and the output face is conical. This element is a new optical element. The spherical face of this element transforms an input collimated laser beam into a convergent beam, which is then transformed into convergent BLB by the conical face.

We investigated how the radius of the central peak of BLB₀ and axial intensity depends on the radius of the collimated beam with a uniform transverse intensity distribution incident on the spherical-conical lens, and also on the focal length f corresponding to the spherical face.

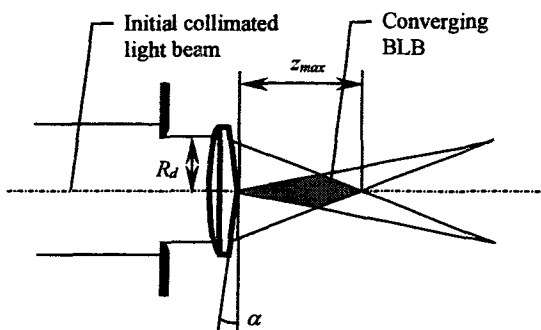


Figure 8. Production of converging BLB.

(more than 10 deg) base angles poses serious technological difficulties. The most convenient for manufacturing are the axicons with base angle of 2-6 deg. We propose a method of production of Bessel light beams with central peak diameters on the order of wavelength by using such axicons.

Converging BLB exists in the region which approximately corresponds to the figure formed by rotating the deltoid shaded in Fig. 8. For an axicon with the base angle α the length of this deltoid is

$$z_{\max} = R_d / (\tan(\arcsin(n \sin(\alpha + \arcsin(\sin(\tan(R_d/f)/n)))) - \alpha)).$$

The radius of the central maximum linearly decreases with z for $z < z_{\max}$, and linearly increases when $z > z_{\max}$.

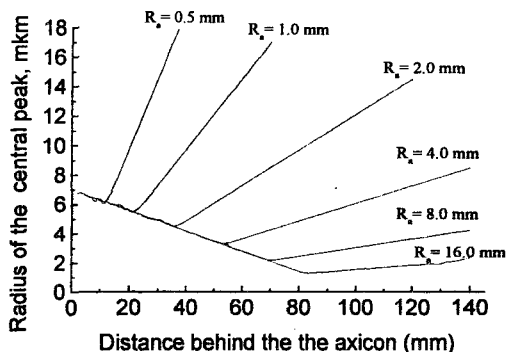


Figure 9. Radius of the central maximum versus longitudinal coordinate z .

Fig. 9 shows the axial dependence of the central peak radius for different values of the radius of the incident collimated beam. It is clear that for given f and α it is possible to achieve the narrowest central peak of BLB₀ by increasing the radius of the incident beam. When $z = z_{\max}$, the amplitude and intensity reaches its maximum value (Fig. 10). Such behavior fulfills the requirements for focusing of atomic beams very well.

It is noteworthy that when the intensity distribution of the initial beam is not uniform (e.g. Gaussian), the amplitude distribution along the optical axis will be different from the distribution shown in Fig. 10.

As for the dependence of the central peak radius on the axial coordinate z for different f , the minimal central peak radius is obtained at decreased distances from the conical lens as the focal length decreases. However, it is not always necessary to achieve a quick decrease of the spot radius when focusing beams of particles. It is sometimes necessary to have a minimal spot radius at larger distances z . In this case

the focused Bessel beams have an indisputable advantage over Gaussian beams, for which the smallest focal spots can be achieved only with lenses having short focal lengths.

We have conducted an experiment to investigate the axial distribution of the central peak width and the maximum intensity on the axis of convergent BLB₀ which was formed from a collimated Gaussian beam (Fig. 11). The experimental results are in full agreement with theoretical predictions.

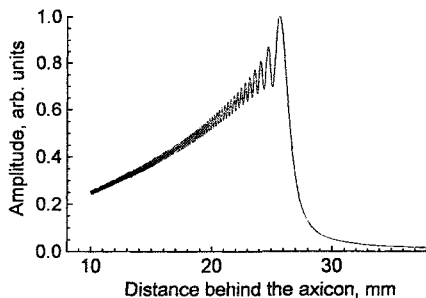


Figure 10. Axial amplitude distribution of focused Bessel light beam ($f = 5$ cm; axicon cone base angle is 4 deg.; $R_s = 2$ mm).

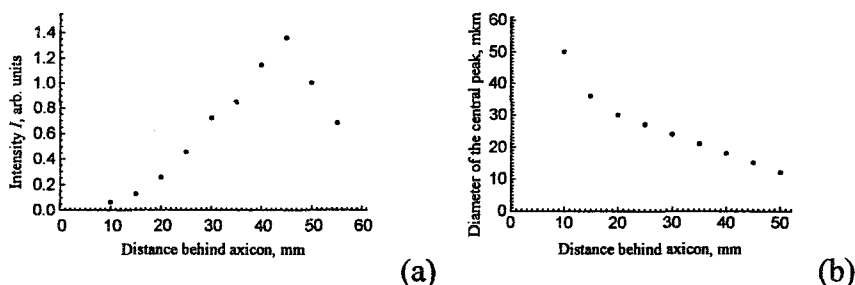


Figure 11. Longitudinal intensity distribution in the 0-th maximum of BLB₀. (a) and diameter of 0-th maximum versus distance from axicon (b).

The radial intensity distribution for any $z < z_{max}$ is always described by the squared Bessel function of the zeroth order when the of initial light beam has axially symmetric intensity distribution and constant phase in its cross-section.

In conclusion, it is necessary to note that the above dependencies on longitudinal coordinate are true for converging BLB₁. Focused BLB₁ provide broader possibilities of controlling the cooled atom beams in comparison with usual BLBs and Gaussian beams.

References

1. Cirac J. I., Zoller P., Quantum computations with cold trapped ions, *Phys. Rev. Lett.* **74** (1995) pp. 4091-4094.
2. Florjanczuk M., Tremblay R., Guiding of atoms in a travelling-wave laser trap formed by the axicon, *Optics Commun.* **74** (1989) pp. 448-450.
3. Arlt J., Hitomi T., Dholakia K., Atom guiding along Laguerre-Gaussian and Bessel light beams, *Appl. Phys. B* **71** (2000) pp. 549-554.
4. Paterson C., Smith R., Higher-order Bessel waves produced by axicon-type computer-generated holograms, *Optics Commun.* **124** (1996) pp. 121-130.
5. Kazak N. S., Khilo N. A., Ryzhevich A. A., Generation of Bessel light beams under the conditions of internal conical refraction, *Quantum Electronics* **29** (1999) pp. 1020-1024.

COMPUTER SIMULATION OF GAS-PHASE PLASMA CHEMISTRY AND SILICON ION CLUSTER FORMATION DURING PECVD

A. F. STEKOLNIKOV, D. V. FESHCHENKO, T. A. METELSKIY, R. F. BELICH

*Belarusian State University of Informatics and Radioelectronics
P. Browka 6, 220027 Minsk, Belarus*

E-mail: labmod@gw.bsuir.unibel.by

The comprehensive gas-phase model of silane (SiH_4) decomposition during plasma enhanced chemical vapor deposition (PECVD) of amorphous silicon including the formation of stable negative hydrogenated silicon ion clusters containing 30 silicon atoms is suggested. The kinetics of the silane decomposition and the reaction products accumulation are computed.

One of the main problems in simulation of chemical vapor deposition from silane plasmas supposes creating an appropriate model of silane decomposition with formation of negative and positive hydrogenated silicon ion clusters.

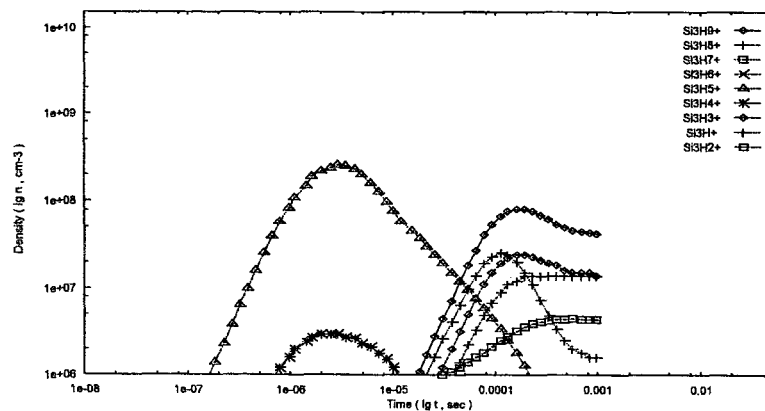
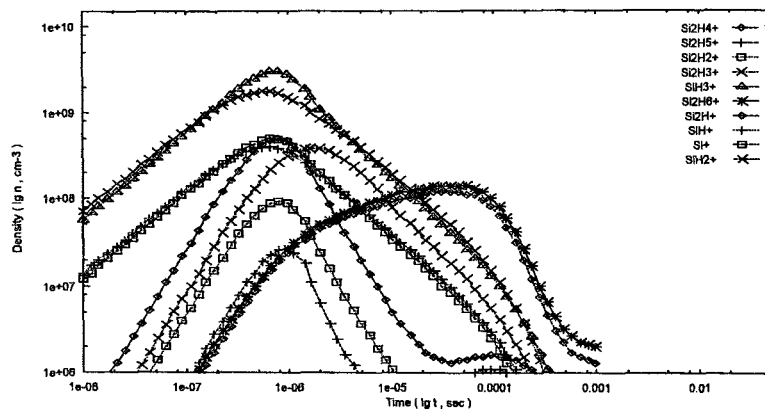
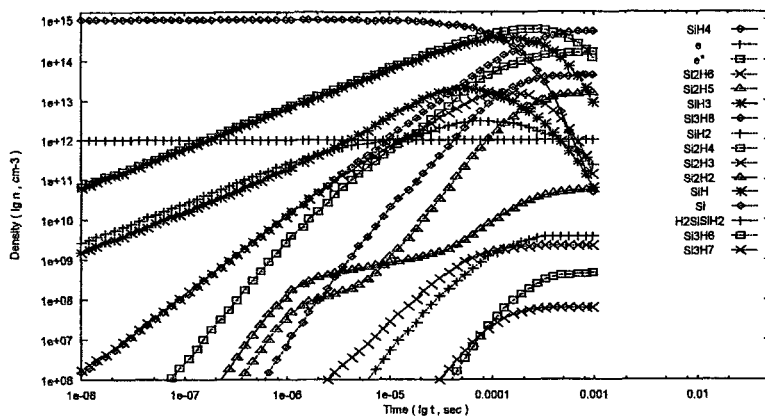
A simulation of particle growth requires a time-dependent modeling of the gas-phase plasma chemistry. Currently, negative ions are believed to be the precursors of silicon dust in SiH_4 plasma. Mass spectroscopy reveals that negative ions can grow up to 60 Si atoms. We have suggested the generalized model of gas-phase reactions of silane decomposition initiated by the electron impact with formation negative (containing up to 30 silicon atoms) and positive (containing 5 silicon atoms) hydrogenated ion clusters. In the kinetic scheme of silane decomposition 219 reactions were included following the sequence of ion-molecular reactions [1-9].

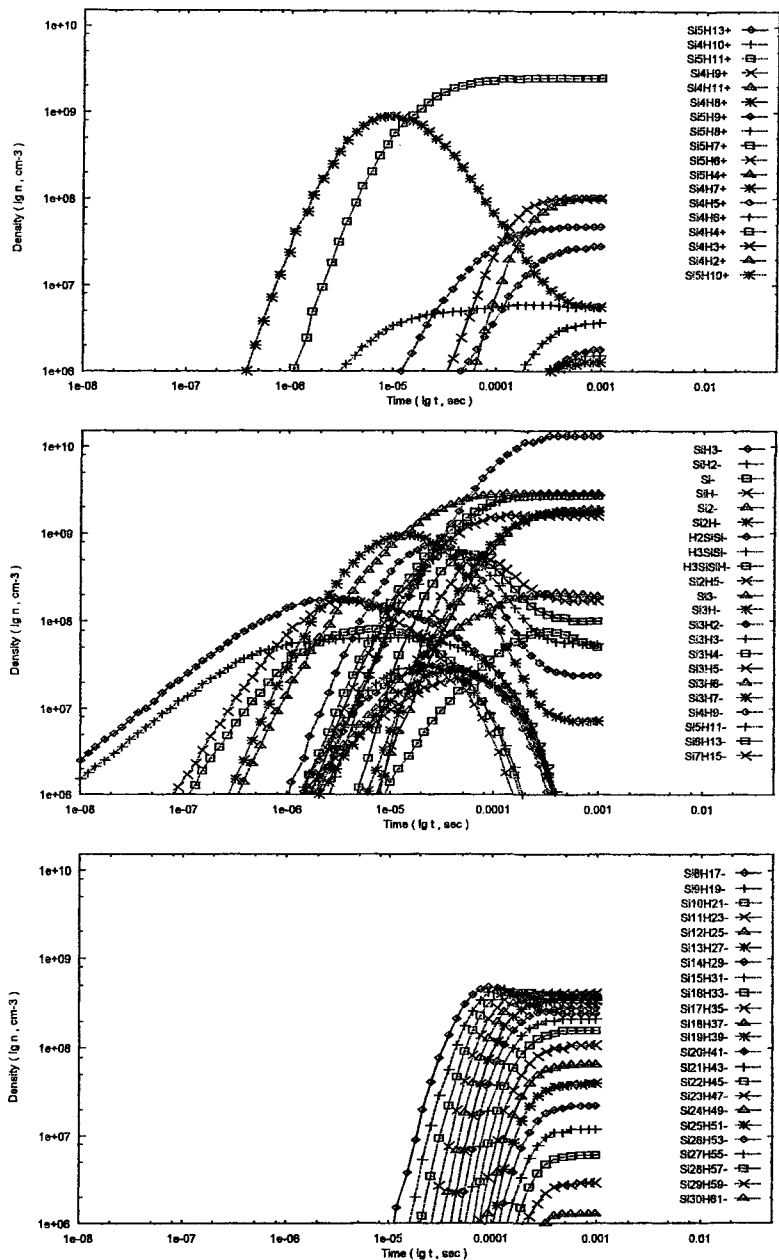
The mathematical model comes to a set of ordinary first-order-differential equations with the given initial conditions, which describe a temporal evolution of formation of both stable products and fast-reacting species:

$$\frac{dN_i}{dt} = \sum_j n_e K_{ij} N_j + \sum_{jl} K_{jl} N_j N_l - N_i \left(\sum_j n_e K_{ji} + \sum_{jl} K_{jl} N_l \right),$$

where n_e is the electron concentration, N_j is concentration of the reaction components, k_{ij} , k_{jl} are the rate reaction constants. The numerical integration of the chemical kinetics equations was done by the Gear's method.

The computed kinetic curves of the silane decomposition to positive and negative hydrogenated silicon ion clusters for silane density $N = 10^{15} \text{ cm}^{-3}$, electron density $N_e = 10^9 \text{ cm}^{-3}$ and electron temperature $T_e = 1.0 \text{ eV}$ are presented in Figs. 1 - 6:





Figures 1-6. Time evolution of species in SiH_4 discharge.

Numerical results on negative hydrogenated silicon ion clusters show the formation of stable negative clusters $\text{Si}_6\text{H}_{13}^-$, $\text{Si}_7\text{H}_{15}^-$, $\text{Si}_8\text{H}_{17}^-$, $\text{Si}_9\text{H}_{19}^-$, $\text{Si}_{10}\text{H}_{21}^-$, $\text{Si}_{11}\text{H}_{23}^-$, $\text{Si}_{12}\text{H}_{25}^-$, $\text{Si}_{13}\text{H}_{27}^-$, $\text{Si}_{14}\text{H}_{29}^-$, $\text{Si}_{15}\text{H}_{31}^-$, $\text{Si}_{16}\text{H}_{33}^-$, $\text{Si}_{17}\text{H}_{35}^-$, $\text{Si}_{18}\text{H}_{37}^-$, $\text{Si}_{19}\text{H}_{39}^-$, $\text{Si}_{20}\text{H}_{41}^-$, $\text{Si}_{21}\text{H}_{43}^-$, $\text{Si}_{22}\text{H}_{45}^-$, $\text{Si}_{23}\text{H}_{47}^-$, $\text{Si}_{24}\text{H}_{49}^-$, $\text{Si}_{25}\text{H}_{51}^-$, $\text{Si}_{26}\text{H}_{53}^-$, $\text{Si}_{27}\text{H}_{55}^-$, $\text{Si}_{28}\text{H}_{57}^-$, $\text{Si}_{29}\text{H}_{59}^-$, $\text{Si}_{30}\text{H}_{61}^-$. Their concentration ranges from $7 \times 10^7 \text{ cm}^{-3}$ up to $8 \times 10^3 \text{ cm}^{-3}$ for the time $5 \times 10^{-4} \text{ s}$.

In conclusion, we have developed the theory of the negative hydrogenated silicon ion clustering in PECVD processes. This investigation continues our preceding work [8].

References

1. Stekolnikov A. F., Feshchenko D. V. In *XX-th ICPIG*, (Pisa, 1991) p. 349.
2. Stekolnikov A. F., Feshchenko D. V., et al. In *XI-th ESCAMPIG*, (St. Petersburg, 1992).
3. Howling A. A., Sansonnens L., et al., *J. Phys. D* **26** (1993) 1003.
4. Hollenstein C., et al., *J. Vac. Sci. Technol. A* **14** (1996) 535.
5. Perrin J., Bohm C., et al. *Plasma Sources Sci. Technol.* **3** (1994) 252.
6. Hollenstein C. et al., *J. Phys. D* **31** (1998) 74.
7. Stekolnikov A. F., Feshchenko D. V., Ivanov O. M., Sergeantov A. S. In *Proc. XIV-th ESCAMPIG* (Dublin, 1998).
8. Stekolnikov A. F., Feshchenko D. V., Ivanov O. M., Sergeantov A. S. In *Physics, Chemistry and Applications of Nanostructures* (World Scientific, Singapore, 1999) 255.
9. Stekolnikov A. F., Feshchenko D. V., Ivanov O. M., Sergeantov A. S. In *Proc. XIV Intern. Symposium on plasma chemistry* (Prague, 1999) 1421.

DEVELOPMENT AND APPLICATION OF NANOSTRUCTURED METALLIZED FIBER MATERIALS IN MICROWAVE ABSORBERS

V. BOGUSH, V. GLYBIN, L. LYNKOV

*Belarussian State University of Informatics and Radioelectronics
6 P. Browka Street, 220027 Minsk, Belarus*

E-mail: aleks@gw.bsuir.unibel.by

Methods for synthesis of nanostructured metallized fiber materials based on the polyacrylonitrile and cellulose modification and ion-exchange reaction are developed. Structure and element analysis of synthesized materials is carried out. It is shown that these materials contain atoms of deposited metals and have microdispersed or disordered cluster structure. Electrical properties of nickel and cobalt containing materials are investigated. Design of multilayers flexible electromagnetic shields and microwave absorbers are presented. Developed microwave absorber has non-resonance frequency characteristic in the frequency range from 1.5 to 118 GHz.

1 Introduction

An increase of the number of radioelectronic devices and the use of complex electromagnetic signals in communication systems requires development of new electronic elements and materials. Nanostructured materials are very promising for development of new devices because of their unusual physical and chemical properties (very high chemical activity, semiconducting electrical conductivity of metals, mechanical properties etc). Nanocrystalline materials have specific properties and structure which can be changed by reduction of the morphological size down to 10 nm and less [1].

Well-known microwave absorbers and shielding materials such as magnetic metals, ferrite and composites have great disadvantages connected with enhanced weight, large thickness and resonance microwave absorption. Also majority of the materials is crisp and may not be used in flexible absorbers.

New types of elastic and flexible shielding and microwave absorbing coatings manufacture as knitted goods from the metal threads or metallized fibers [2]. Lightweight absorbers with decreasing thickness may be formed from fibers containing inorganic clusters in a polymer matrix.

It is shown that metal nanosize particles in the polymers fiber are formed by the methods of chemical modification of polyacrylonitrile and cellulose with deposition of the metal ions from aqueous solutions [3]. These methods permit to create materials containing metal-polymers and inorganic clusters with narrow size distribution what was shown by the X-ray analysis.

In the present paper we report experimental results of structure and electromagnetic properties of fiber materials containing nickel and cobalt clusters and their use in the ultra-thin flexible microwave absorbers and electromagnetic shields.

2 Methods

The technology for formation of metal composite materials with special structure is designed on the basis of modifying of polyacrylonitrile and cellulose fibres. Method of metal clusters formation bases on the chemical sorption, ion exchange reaction and reduction of metal ions by hydrazinehydrate, borohydrides, etc. Formed metal clusters are centers of advanced metallization by chemical deposition of metals from aqueous solutions. In our work we used polyacrylonitrile fibers with increased sorption capacity of nickel and cobalt ions. The restoration of the sorbed metal ions was carried out by the $\text{Na}_2\text{S}_2\text{O}_4$ treatment. The temperature of deposition was not over the limit of 80 °C. Amount of the deposited metal is up to 10 wt. %.

The nickel and cobalt containing materials were studied by the X-ray diffraction, Auger spectroscopy and X-ray fluorescent analysis. It is shown that the crystallites in fibers include Ni and Co atoms and have a dimension about several nm. Microdispersed structure of the obtained materials sets by the results X-ray analysis.

Electromagnetic properties of the coatings from the metal containing fibres were investigated in 1.5-118 GHz frequency range by the technique using vector network analyzer. The sample is a piece of the knitted cloth from metallised fibres. Conductivity of such materials varies from 10^{-5} to 10^2 Ohm m and depends on the amount of deposited metal.

3 Results and discussion

The frequency characteristics of a single-layer knitted coating starting from 25 GHz have non-resonance mode. They are different for materials with Ni clusters and materials with Co clusters.

Ni containing coatings have a reflection coefficient of about -5 dB and reduce the power of electromagnetic radiation up to the 10^5 times. The cloth with the Co containing fibers reduces the radiation 10 times and has a reflection coefficient about -20 dB what means that more than 95 % of microwave power is absorbed by the material.

We developed a base structure of coatings for microwave absorbing which includes two layers: the first (non-reflecting) layer is made of the fibre containing cobalt submicron clusters, the second (working) layer provides reducing of electromagnetic radiation and based on the nickel containing fibre. Transmitting and absorbing characteristics of the construction are presented in Fig. 1. The

characteristics of the absorbers do not depend on polarization of electromagnetic radiation.

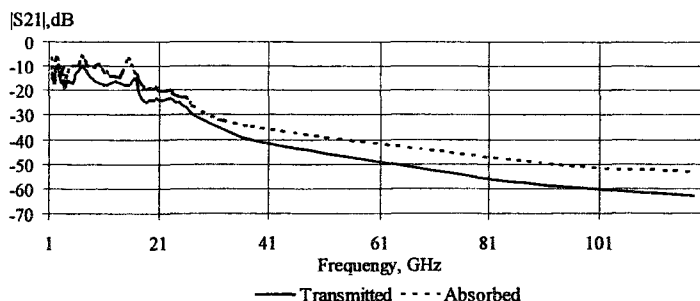


Figure 1. Frequency characteristic of reducing of the microwave power by the two-layer coating from the Ni and Co cluster containing fibers.

4 Conclusion

New materials and design for flexible microwave absorbers were developed. Structure features of fibers with deposited Ni and Co were investigated. Electromagnetic frequency characteristics of the materials were measured.

References

1. Kozinkin A., Vlasenko V., Gubin S., Shuvaev A., Dubovcev I., Clusters in polymeric matrix, *Zhurn. Neorg. Khim.* **32** (1995) pp. 422-428.
2. Bogush V. A., Glybin V. P., Lynkov L. M., Flexible construction of electromagnetic shields (BSUIR, Minsk, 2000).
3. Bogush V., Glybin V., Lynkov L., Synthesis of inorganic nanoparticles in fiber polymers and their properties. In *Physics, Chemistry and Application of Nanostructures*, ed. by Borisenko V. E., Gaponenko S. V., Filonov A. B., Gurin V. S. (World Scientific, Singapore, 1999) pp. 251-254.

NANOSTRUCTURE BASED DEVICES

This page is intentionally left blank

INVITED

CARRIER TRANSPORT AND ELECTROLUMINESCENCE IN Si/CaF₂ SUPERLATTICES

V. IOANNOU-SOUGLERIDIS, A. G. NASSIOPOULOU

*Institute of Microelectronics NCSR "Demokritos"
P.O. Box 60228, 153-10, Aghia Paraskevi Athens Greece*

E-mail: A.Nassiopoulou@imel.demokritos.gr

T. OUISSE

*LPCS, UMR CNRS 5531, ENSERG
23 rue des Martyrs, 38016, Grenoble, France*

E-mail: Ouisse@enserg.fr

F. BASSANI, F. ARNAUD D'AVITAYA

*CRMC2-CNRS
Campus de Luminy Case 913, 13288 Marseille, Cedex 9, France*

E-mail: bassani@crmc2.univ-mrs.fr

In this paper, different factors which influence carrier transport in Si/CaF₂ multi quantum wells and superlattices are reviewed. It is shown that when CaF₂ thickness in each period is above ≈ 1 nm Si/CaF₂ multilayers behave as an insulating structure. Charge exchange between the silicon substrate and Si/CaF₂ layers occurs, giving rise to impedance frequency dependent effects. Carriers injected into the multilayers are trapped and form a space charge region near the injecting interface. The conduction mechanism seems to be thermally activated above 200 K, involving a continuous distribution of trapping levels in the range of 0.3-0.8 eV. In the superlattices with CaF₂ below 1 nm, a Poole-Frenkel mechanism of carrier transport has been demonstrated at temperatures below 280 K. At higher temperatures, an important increase of current through the layers is observed above a threshold voltage of 4-5 V, which is accompanied by hysteresis effects and current instabilities probably involving structural changes of the material. Electroluminescence is observed under these conditions, with a spectrum similar to those of photoluminescence.

1 Introduction

Silicon nanocrystals have been widely studied for their interesting optical and electrical properties, such as room temperature photoluminescence and electroluminescence in the visible range [1]. These properties are considered to arise from quantum confinement of carriers within the silicon nanocrystals. In addition, it has been demonstrated that surface passivation of the nanocrystals and the atomic species occupying dangling bonds at the surface, play an important role

in their electronic properties [2]. Different methods were successfully used to fabricate structures containing Si nanocrystals in different matrices. Special attention has been given to the fabrication of Si/SiO₂ superlattices, due to the compatibility of SiO₂ with integrated circuit fabrication and its excellent isolating properties (energy gap 9.1 eV) [3-6].

Calcium fluoride (CaF₂) is an alternative insulator instead of SiO₂. Si/CaF₂ superlattices are grown by molecular beam epitaxy (MBE) and the Si layer thickness is thus controlled with a high precision [7]. CaF₂ is a wide band gap crystalline material with energy gap of 12.1 eV. Multilayer (ML) structures consisting of many alternating layers (typically 50 or 100 bilayers) of low dimensional Si and CaF₂ layers have been successfully synthesized by MBE at room temperature [7]. The low temperature growth process leads to the formation of nanocrystalline layers, which exhibit visible photoluminescence at ambient temperature, if the Si layer thickness is below 2.5-3 nm. These structures show also electroluminescence by applying an electric field in a direction vertical to the layers [8]. In this work we review the effects which influence transport properties of these Si/CaF₂ MLs and we also show recent electroluminescent results from these structures.

2 Experimental results and discussion

2.1 Electrical characteristics

The electrical characteristics in a vertical structure of Si/CaF₂ multilayers were found to depend strongly on the CaF₂ layer thickness in each period. Samples with CaF₂ thickness larger than 1 nm, behave almost as insulators and the current through the layers is very small. Samples with CaF₂ thickness below 1 nm show significant currents through the layers. These samples are in general electroluminescent.

2.1.1 Si/CaF₂ structures with CaF₂ thickness in each bilayer above 1 nm (Multi Quantum Wells MQWs)

Fig. 1(a) shows a typical C-V characteristic at 1 MHz of the sample with 50 periods and $t_{\text{CaF}_2} = t_{\text{Si}} = 1.6$ nm. The general behavior of the C-V plot is similar to that of a metal-insulator-semiconductor (MIS) capacitor with regions of accumulation, depletion and inversion. Two characteristic features are evident: a) the change in capacitance in the depletion region is abrupt, with no significant stretch-out; b) a large hysteresis is evident during the return sweep. The extent of the hysteresis indicates that a significant amount of charges are trapped within the ML stack. For this particular case the trapped charge was found to be $Q_t = 2.5 \times 10^{-12}$ C. Also the direction of the hysteresis, which is clock-wise indicates that this is related to charge injection from the silicon substrate and subsequent trapping within the

structure. Detailed measurements showed that in accumulation electron injection occurs, while in inversion hole injection is dominant.

Charge injection within the MQWs is also confirmed by the observed frequency dispersion in accumulation. Fig. 1(b) illustrates this effect, which is more pronounced in accumulation. When the CaF_2 layer thickness in each bilayer increases, the dispersion is reduced. At high enough frequencies, charges are not able to respond to voltage modulation, while they have time to move within the layers at lower frequencies [9].

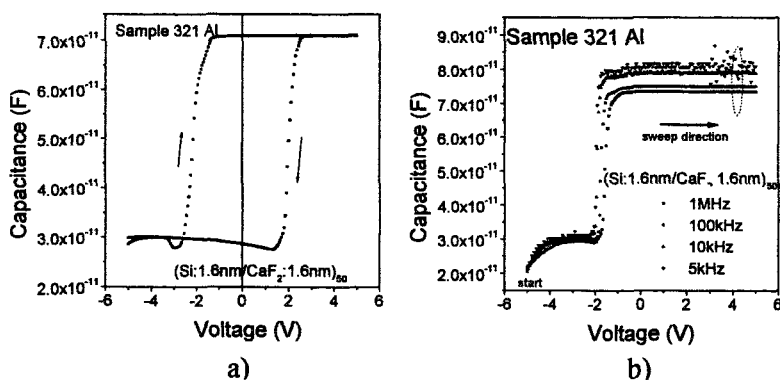


Figure 1. a) Capacitance-voltage characteristics of the MQW structure $[\text{Si:1.6 nm}/\text{CaF}_2:1.6 \text{ nm}]_{50}$ on Si(111) substrate. b) Frequency dispersion of C-V curves of the same sample.

From the conductance peaks it is possible to estimate the “effective” interface trap density D_{it} . This density involves in fact not only states at the interface but also states within the layers [9]. Typical values of D_{it} were in the range of 5×10^{11} – $5 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$. These values are in general comparable with those we obtain in the case of SiO_2 on Si(111) which are higher than those of SiO_2 on (100) silicon. The absence of a significant stretch-out effect despite the large values of the interface trap density can be explained by the fact that at high temperatures the carriers are able to escape from the interface states resulting in a non thermal equilibrium between interface and substrate [10]. Significant stretch-out has been seen, indeed, only at low temperatures [9].

Fig. 2(a) shows the Arrhenius plot of the temperature dependence of the dark current from a sample with $t_{\text{CaF}_2} = 3 \text{ nm}$ and $t_{\text{Si}} = 1.5 \text{ nm}$ for several gate voltages. The current is very low, below 10^{-12} A , and starts to increase above 180 K. The Arrhenius plots are non-linear, especially in the temperature range of 180–250 K. A narrow hump exists also in the curves at around 250 K, separating the Arrhenius plot in two regions. From the slopes of the Arrhenius plots the activation energy was found to increase with temperature, having values in the range of 0.3–0.7 eV. It has been suggested that the non-linearity of the Arrhenius plot indicates a distribution of trapping levels within the structure and/or a tunneling process

between traps [11]. However, the quite large activation energies rule-out the tunneling process, and the existence of a distribution of trapping levels within the material seems more probable.

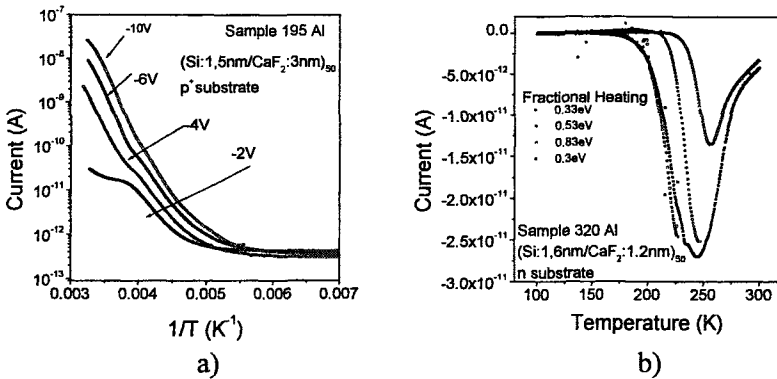


Figure 2. a) Temperature dependence of the dark conductivity of the sample composed of 50 bilayers, with $t_{\text{CaF}_2}=3$ nm and $t_{\text{Si}}=1.5$ nm, deposited on a p^+ substrate. b) TSDC fractional heating method. The method reveals that the TSDC peak is due to carriers trapped in a continuous distribution of states.

The thermally stimulated detrapping current (TSDC) was also employed for samples with CaF_2 thickness in each bilayer above 1 nm [12]. The resulted peaks shown in Fig. 2(b) are extremely broad indicating the existence of a continuous distribution of trapping levels. This point was further investigated by the fractional heating method. The most important result is the continuous increase of the activation energy from 0.3 to 0.5 eV and finally to 0.8 eV, consistent with the above indication that a distribution of defects exists within the MLs.

The above results showed that Si/CaF_2 multilayers with CaF_2 layer thickness in each bilayer >1 nm and Si thickness around 1.5 nm, with a total number of periods equal to 50 or 100 have the following characteristics:

- The multi-layer stack behaves like an insulator.
- Charge exchange between the Si substrate and the Si/CaF_2 layers occurs, giving rise to impedance frequency dependent effects.
- Carriers are injected into the multilayers where they are trapped allowing the formation of a space charge region near the injecting interface.
- The conduction mechanism seems to be thermally activated above 200 K involving a continuous distribution of trapping levels ranging from 0.3 to 0.8 eV.

2.1.2 Si/CaF_2 superlattices (CaF_2 thickness in each period below 1 nm)

Electrical properties of samples with thin CaF_2 layers in each period exhibit different behaviour. A current increase with time is observed when a positive

voltage is applied to the top electrode. This effect is so extended, that it produces noticeable changes between the up and down sweep of the I-V characteristic as it can be seen in Fig. 3(a). This current increase with time results finally in high current densities through the structure, of the order of 1 A/cm^2 and it is usually accompanied by light emission. The time evolution of the effect can be seen in Fig. 3(b) for 3 virgin devices taken from a sample consisting of 100 periods with CaF_2 layer thickness equal to 0.56 nm and Si layer thickness equal to 1.6 nm grown on a silicon (111) n^+ substrate. The gate metal was semitransparent gold. When the gate voltage becomes 7 V or higher the current increases by 10^5 orders of magnitude. Once this effect sets in, memory effects are observed in the current-voltage characteristics.

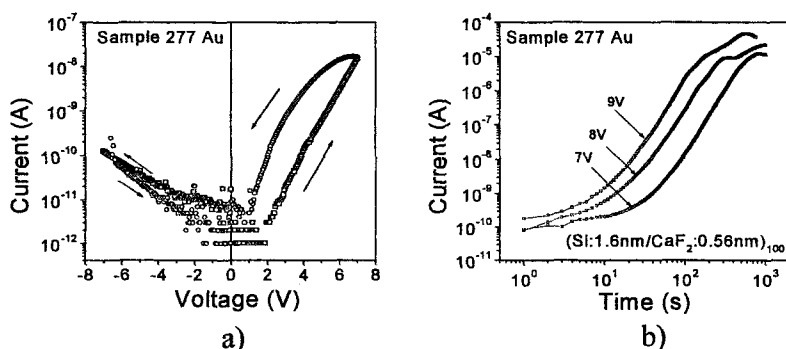


Figure 3. a) I-V characteristics of the nc-Si/ CaF_2 superlattice. b) Time evolution of the current for three different gate voltages.

This huge increase of the conductivity with time implies a radical and permanent change of the electrical properties of the superlattice. This behaviour shows many similarities with a phenomenon known as “forming” observed in amorphous oxide and fluoride films. “Forming” occurs by applying to the material a voltage above some critical value. Before being “formed” the material is an insulator, afterwards it switches to a conducting state, which exhibits NDR and electroluminescence [13]. “Forming” occurs more readily in insulators with reactive anions such as fluorides (CaF_2 MgF_2 MnF_2) and appears to be easier when the insulator is non-stoichiometric [12]. The models developed to explain this effect involve either the creation of space charge with conduction via impurity states or a combination of electronic and ionic motion [13]. Another model explains these changes assuming filamentary conduction, created at weak points of the insulator. Since many experimental characteristics of the “forming” process are common to our Si/ CaF_2 superlattices, we tend to conclude that this rather unusual behaviour of the current increase with time in the SLs is also due to structural modifications of the material.

At temperatures below 280 K this effect of current increase with time was found to be insignificant within the time scale of the measurement. The absence of any significant hysteresis allowed the study of the transport properties. The current-voltage and current-temperature characteristics suggested a Poole-Frenkel type mechanism of carrier transport through the SLs (Fig. 4(a)). It has been demonstrated that even with the presence of the large electrostatic potential induced by the SLs, the current behaviour was not expected to depart from the simple Poole-Frenkel model, except at extremely large electric fields (in excess of 0.2 MVcm^{-1}) [14].

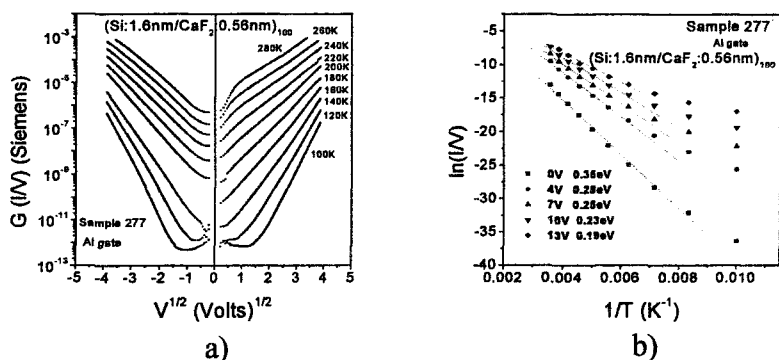


Figure 4. a) Conductance ($G=I/V$) vs $V^{1/2}$ at selected temperatures. At gate voltages higher than 64 V the characteristics are linear and symmetrical, suggesting a Poole-Frenkel mechanism. b) Arrhenius plot of the conductance for several applied voltages.

Transport was dominated by thermal emission from traps characterized by an activation energy of 0.35 eV at zero electric field (Fig. 4(b)). Thus, the experimental data indicate that transport in these Si/CaF₂ superlattices is dominated by the presence of defects. However, the reduced CaF₂ thickness eliminates most of the slow trapping phenomena, which are observed in thick structures.

2.2 Electroluminescence

Electroluminescence is detected only from nc-Si/CaF₂ superlattices (with CaF₂ layer thickness in each period below 1 nm). EL is observed with a positive gate voltage applied on the top semitransparent electrode (ITO or Au). When the gate voltage exceeds a critical value around 4-5 V the current starts to increase. At a current density approximately 1 A/cm^2 a low-level red-orange electroluminescence is observed and easily detectable with naked eye in the dark. During the initial increase of the current no measurement is performed. At high current densities the current stabilizes and is almost constant. At this point the electroluminescence spectra are recorded.

Fig. 5(a) shows a typical PL spectrum from an as-grown sample, aged in air, consisting of 100 periods of Si/CaF₂, with CaF₂ layer thickness in each period equal

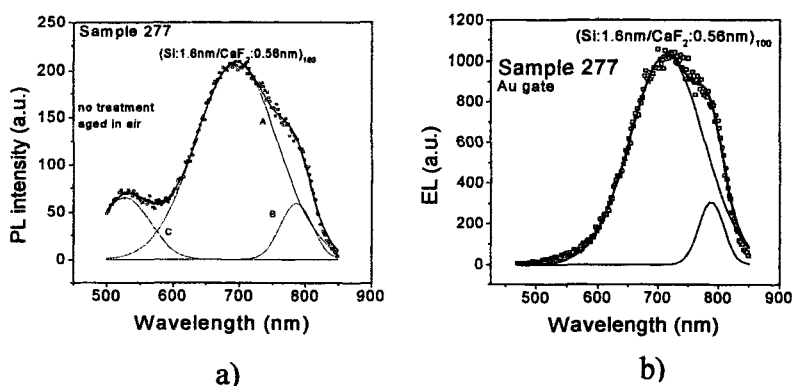


Figure 5. a) Room temperature PL characteristics of a sample consisting of 100 bilayers, having Si layer thickness 1.6 nm and CaF₂ layer thickness 0.56 nm. The experimental points can be fitted assuming three gaussian peaks. b) Electroluminescence spectra for several current levels from the same structure.

to 0.56 nm, and Si layer thickness equal to 1.6 nm grown on a silicon (111) n^+ substrate. The PL emission consists of three bands. Assuming that they follow a gaussian distribution, the spectrum can be composed of three peaks shown in Fig. 5(a). The dominant peak A is located at 690 nm (1.8 eV), while the two side bands B and C at 760 nm (1.6 eV), and 550 nm (2.25 eV), respectively. Peaks A and B are attributed to the radiative recombination of electrons and holes within the Si crystallites, while peak C is attributed to defects.

Fig. 5(b) shows EL spectra from the same sample, having a semitransparent Au gate, for several injection current levels. As evident from Figs. 5(a,b) the EL and the PL signals show identical characteristics and only the high-energy peak C is missing from the EL spectra. Moreover, EL measurements performed on the same sample with an ITO electrode gave identical results. The origin of PL and EL is carrier localization within silicon nanocrystals, the recombination mechanism involving states within the gap, influenced by surface passivation and disorder within the material.

3 Conclusion

Electroluminescence from silicon nanocrystals in Si/CaF₂ superlattices shows similar spectral characteristics as photoluminescence from the same structures, attributed to carrier localization within the semiconducting nanocrystals, with recombination involving electronic states within the gap, arising from surface passivating species and/or disorder. EL is observed only if an important current,

above 1 A/cm^2 passes through the layers, which occurs for a stack of 50 or 100 periods when CaF_2 thickness in each period is below 1 nm, at a voltage of 4-5 V.

4 Acknowledgements

This work has been financially supported by the EU Project MEL-ARI SMILE No 28741.

References

1. Kovalev D., Heckler H., Posisski G., Koch F., *Phys. Stat. Sol.* **215** (1999) 871.
2. Workin M. V., Jorne J., Fauchet P. M., Allan G., Delerue C., *Phys. Rev. Lett.* **82** (1999) 197.
3. Lu Z. H., Lockwood D. J., Baribeau J.-M., *Nature* **378** (1995) 258.
4. Tsybeskov L., Grom G. F., Jungo M., Montes L., Pauchet P. M., McCaffrey J. P., Baribeau J.-P., Sproule G. I., Lockwood D. J., *Mat. Sci. Eng. B* **69-70**, (2000) 303.
5. Photopoulos P., Nassiopoulou A. G., Kouvatsos D. N., Travlos A., *Appl. Phys. Lett.* **76** (2000) 3588.
6. Photopoulos P., Nassiopoulou A. G., *Appl. Phys. Lett.* **77** (2000) 1816.
7. Bassani F., Vernoot L., Mihalcescu I., Vial J.C., Arnaud d'Avitaya F., *J. Appl. Phys.* **79** (1996) 4066.
8. Ioannou-Sougleridis V., Tsakiri V., Nassiopoulou A. G., Photopoulos P., Bassani F., Arnaud d'Avitaya F., *Phys. Stat. Sol.* **165** (1998) 97.
9. Ioannou-Sougleridis V., Tsakiri V., Nassiopoulou A. G., Bassani F., Menerd S., Arnaud d'Avitaya F., *Mat. Sci. Eng. B* **69-70** (2000) 309.
10. Liss B., Engstrom O., *J. Appl. Phys.* **78** (1995) 1824.
11. Jauhiainen A., Bengsson S., Engstrom O., *J. Appl. Phys.* **82** (1997) 4966.
12. Ioannou-Sougleridis V., Nassiopoulou A. G., Ciurea M. L., Bassani F., Arnaud d'Avitaya F. In *Abstract book of E-MRS* (Strasbourg, France, 2000).
13. Dearnaley G., Stoneham A. M., Morgan D. V., *Rep. Prog. Phys.* **33** (1970) 1129.
14. Ioannou-Sougleridis V., Ouisse T., Nassiopoulou A. G., Bassani F., Arnaud d'Avitaya F., *J. Appl. Phys.* **89** (2001) 610.

INVITED

REVERSE BIASED POROUS SILICON LIGHT EMITTING DIODES FOR OPTOELECTRONICS

S. K. LAZAROUK

Belarusian State University of Informatics and Radioelectronics

P. Browka 6, 220013 Minsk, Belarus

E-mail: serg@nano.bsuir.edu.by

An overview of reverse biased porous silicon (PS) light emitting diodes (LEDs) is presented. Emphasis is given to LED designs and technological processes for PS fabrication. Basic parameters of PS LEDs are analyzed with particular attention to their application in optoelectronics. A silicon integrated optoelectronic unit including a reverse biased PS LED connected with a photodetector by an alumina waveguide is considered for intra-chip optical interconnects. The other use the reverse biased PS LEDs in microdisplay devices is also discussed. Advantages and disadvantages of PS LEDs for optoelectronics are exposed.

1 Introduction

Silicon is a basic material in microelectronics. However, bulk silicon is an indirect gap semiconductor which makes it inefficient in emitting light. Therefore, silicon has limited optoelectronic applications, as compared to direct gap semiconductors.

In the last years, porous silicon based light emitting diodes have been extensively studied because of room temperature electroluminescence, which raises hopes of an all silicon based optoelectronics. The first PS LED was reported in 1991 [1]. It emitted light at both forward and reverse biases. At present, more than 200 papers dealing with PS LEDs have been published. They are mostly dedicated to light emission at forward bias. However the best efficiency and frequency parameters have been observed for reverse biased devices [2,3], while published reviews [4] deal mainly with forward biased PS LEDs. The state of the art for reverse biased PS LEDs is first reviewed in this paper.

2 State of the art

The first reverse biased PS LED was demonstrated by German group (Richter et al. [1]) in 1991. A PS layer was formed on an n-type silicon substrate. Then, a semitransparent gold electrode was deposited upon the PS layer in order to form the Schottky barrier between the gold electrode and the PS layer. Light emission was observed in the visible range with the peak at 650 nm. The quantum efficiency was

in the range of $10^{-5} - 10^{-6}$ [1,5]. The lifetime of such reverse biased PS LEDs varied from 45 min to 100 h, after which the parameter degradation and emission attenuation took place [1,5,6].

A significant improvement in the efficiency and stability was made by the Belarussian – Italian research group (Lazarouk et al. [2]) in 1995 through the formation of the oxidized PS layer protected from atmospheric oxygen by an additional passivation layer. The oxidized PS layer was formed on low resistivity n-type silicon by anodization in the transition regime [7], providing a continuous anodic oxide on the surface [8]. Moreover, the additional passivation layer of transparent anodic alumina was formed on the PS layer by a selective aluminum anodization in an oxalic electrolyte during formation of the aluminum Schottky electrode. The passivation ensured the stability of continuous PS LED operation during 1000 h without degradation effects. The quantum efficiency for oxidized PS LEDs was in the range of $10^{-4} - 10^{-3}$ [2,9].

In 1998, the Australian group (Kuznetsov et al. [10]) improved the PS LED design developed by the above-mentioned Belarussian – Italian group in order to enhance the device efficiency. In particular, they have replaced the opaque aluminum electrode with a semitransparent silver electrode. The efficiency of this reverse biased PS LED was about 0.5×10^{-2} [8].

Recently the more efficient reverse biased PS LEDs have been reported by the Japan group (Gelloz et al. [3,11]). The quantum efficiency of about 10^{-2} has been obtained by the modified technology for oxidized PS. Porous layer was formed on n⁺-type silicon at 0 °C. Thereafter, the PS layer without drying was electrochemically oxidized by anodization in an aqueous solution of sulfuric acid. The Schottky barrier was formed by a transparent indium – tin – oxide deposition. The advancement of the anodization process by this way decreased the size of nonconfined silicon nanocrystallites in PS. The enhanced quantum efficiency can be explained by primary reduction of leakage carrier flow through the non-confined silicon nanocrystallites [11].

On their way to the advanced reverse biased PS LEDs, which is shown in Fig. 1 all the research groups drew on the earlier experience in upgrading the device design or fabrication processes. So, all the above-mentioned devices have common details or technological features. Specifically, all reverse biased PS LEDs are formed on n-type silicon substrates. It can be explained by the higher Schottky barrier for n-type silicon compared to p-type material [12]. In addition, n⁺-type silicon substrates are preferable because of minimum series resistance of PS LEDs; and since 1995, the research groups employed this material for the device fabrication. The technological process of PS formation must provide a homogeneous size distribution of the confined silicon nanocrystallites at the thickness of porous layer down to 1 μm [2,3,10]. For this reason, the oxidized PS layer was applied in the device fabrication and the temperature of the PS formation was chosen to be 0 °C [3].

In addition to the above mentioned PS LEDs, other approaches are to be considered. Though these approaches have not shown the best parameters, they demonstrate that the PS LEDs can be fabricated on different silicon layers and different substrates. Thus, reverse biased PS LEDs were formed on polysilicon [13] and amorphous silicon [14] layers. Also, PS layers for reverse biased LEDs can be fabricated avoiding electrochemical anodization by stain chemical etching [15]. Furthermore, it is important to mention that reverse biased PS LEDs were formed on transparent substrates such as sapphire [16] and glass [14]. The wide variety of initial substrates and silicon layers are especially important for practical applications, which will be considered in the next sections.

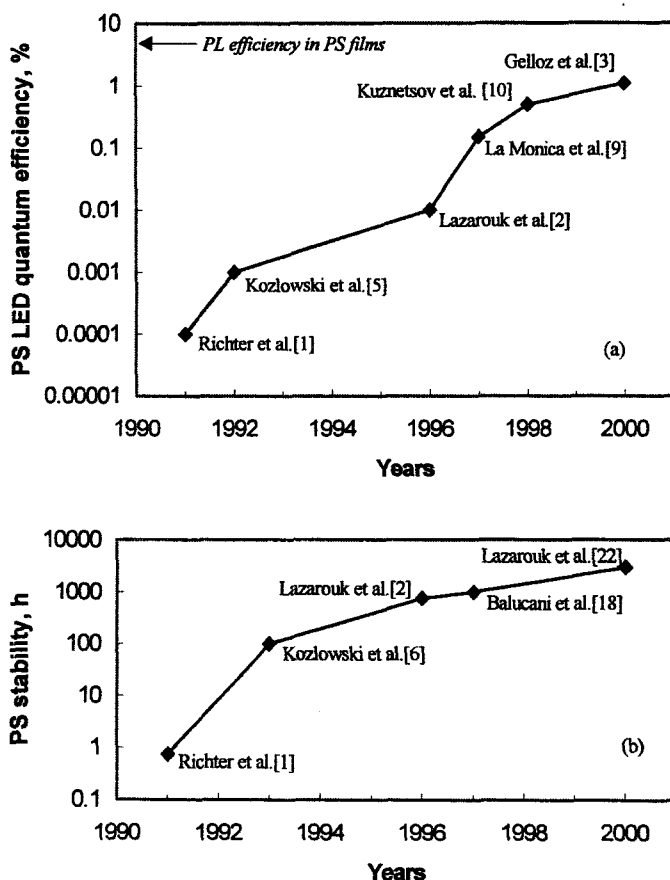


Figure 1. Efficiency (a) and stability (b) progress for reverse biased PS LEDs.

3 Reverse biased PS LEDs for optical intra-chip interconnects

The latest advances in communication systems and computer technology make it increasingly attractive to substitute electrons by photons in transmission and processing of information. Thus, optoelectronic interconnects are required for the next generation of integrated systems. Since the discovery of efficient light emission from porous silicon, this material is considered to be promising for integrated silicon based optoelectronic systems able to emit, transmit, and detect light in the visible range.

The analysis of LED parameters for optical interconnects has been carried out in [4]. Most of the parameters meet the requirements. For example the threshold voltage and current density were 4 V and 0.02 mA/cm² respectively [10,13]. The light emission power density reached 1 W/cm² at pulse excitation [17]. Reverse biased PS LEDs could be operated at a frequency of 200 MHz [18].

However, nowadays the main challenge for implementing PS LEDs in optical interconnects is their low efficiency. As noted in [4], the external LED efficiency of about 10⁻¹ is the required level for optical interconnects. But taking in the account that intra-chip optical interconnects as apposed to inter-chip analogs are operated at a short distance usually less than 1-2 cm, the desired LED efficiency for this application can be at least one order less. So, the reverse biased PS LEDs are more attractive for intra-chip optical interconnects on silicon. Our recent results pertinent to the reverse biased PS LEDs for intra-chip optical interconnects will be presented in this section.

The main technological steps are described elsewhere [2,19,20]. A schematic cross-section of the developed optoelectronic unit based on the reverse biased PS LEDs is shown in Fig. 2(a). Fig. 2(b) presents an equivalent scheme of this unit. It is composed of two Al/PS Schottky junctions and an alumina layer between them. One of the junctions operates as a LED, another - as a photodetector (PD). The distance between them is 10 μm. The anodic alumina protects the porous silicon surface from atmospheric oxygen. Moreover, it plays one more important role in the device. The light emitted by one of the Schottky junctions is transmitted within the alumina layer as in an optical waveguide. As far as the refractive index of porous silicon (1.3-1.6) is lower than that of alumina (1.65-1.77), the anodic alumina layer provides an appropriate light guiding effect. The niobium film acts as a reflector, which assists light spreading within the anodic alumina layer, as it illustrated in Fig. 2(a).

When the left Schottky junction is biased approaching to the avalanche breakdown, and reverse current (I_{LED}) passes through it, light emission can be seen around the aluminum electrode. Meantime, the reverse current appears in the right Schottky junction operating in a photodetector mode. The current through this junction is increased with an increase of I_{LED} as it is depicted in Fig. 3. The similar behavior is observed at increasing of external light intensity. So, we conclude that the measured current is a photo response of the right Schottky junction.

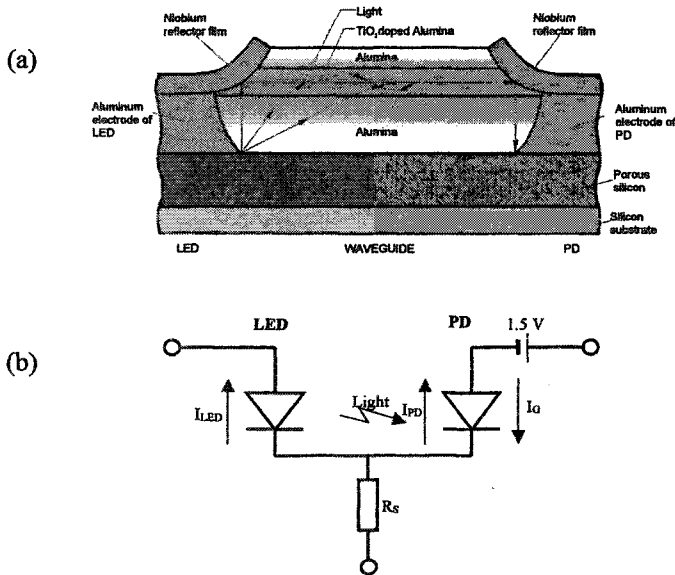


Figure 2. Schematic cross-section (a) and equivalent electric scheme (b) of the integrated optoelectronic unit based on reverse biased PS LEDs.

There is a galvanic link between the LED and the PD (see Fig. 2(b)). However, the direction of the galvanic current (I_G) is opposite to the measured PD current (I_{PD}). To reduce the influence of the galvanic current, we used an additional 1.5 V battery connected with the PD, as shown in Fig. 2. Besides, the substrate resistance (R_S) is about 10 Ω , and simple calculation shows, that for I_{LED} less than 100 mA I_G can not change the PD bias. But for the I_{LED} above 100 mA, the I_G affects the PD bias, thus resulting in the decrease of the I_{PD} values. The relationship between I_{PD} and I_{LED} is close to quadratic dependence. Meantime, the relationship between LED electroluminescence and I_{LED} is also quadratic [21]. It supports the conclusion that the PD response originates from the LED light emission.

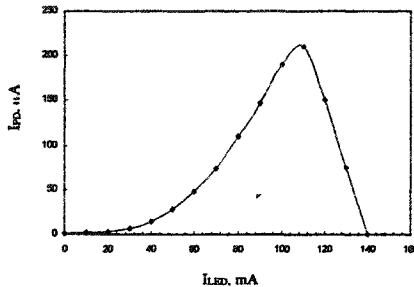


Figure 3. PD current versus LED current in the porous silicon based optoelectronic unit with 10 μ m alumina waveguide between LED and PD.

The ratio of I_{PD} to I_{LED} amounts to 0.19 %. This value can be considered as a minimum quantum efficiency of the developed LED. It should be noted that the developed optoelectronic unit still has perspectives to be further optimized in order to reduce optical losses in the waveguide and to increase the PD signal. This work is in progress.

The special attention has been paid to the time response of the LED [22]. The transient electroluminescence waveform with the minimized time response is shown in Fig. 4. This curve corresponds to the lowest of the series resistance and capacitance in the developed LED. The basic feature of the transient electroluminescence can be characterized by the delay time (time between the application of the drive pulse and the start of the light response) and the rise time. The delay time of 1.2 ns and the rise time of 1.5 ns can be evaluated from the curve presented in Fig. 4 for the voltage pulse of 12 V.

The shortest time response is observed for the maximum bias applied, as it was also described in [23] for forward biased porous silicon LEDs. However, our electroluminescence devices are faster in comparison with the forward biased porous silicon LEDs, because they have no diffusion capacitance, which limits the time response of the light emission. The main mechanism of minor carrier generation in the light emission from reverse biased junctions is impact ionization at avalanche breakdown. For the avalanche breakdown to take place, a high value of electric field is necessary. A regular columnar structure of porous silicon promotes the avalanche breakdown due to non-uniform electric field distribution inside the porous layer [7]. The effect of the impact ionization at the avalanche breakdown is very fast. For example, the time of the avalanche response is estimated to be about 1 ps [12]. The faster carrier generation mechanism results in the shorter time response of our devices as compared to the forward biased porous silicon LEDs.

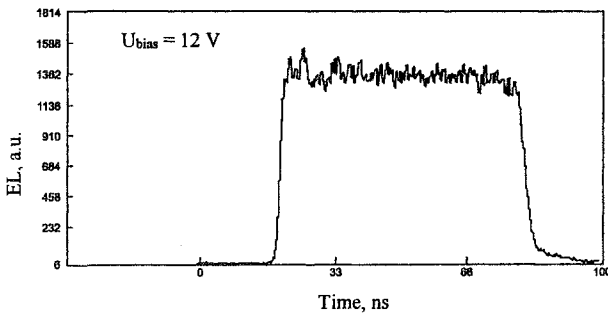


Figure 4. Electroluminescence time response of the porous silicon avalanche LED.

Thus, we have shown that the developed LED can operate in the nanosecond range. It should be noted that these values are not limited for these devices. By further technology optimization, we hope to reach the subnanosecond range, that is promising for LED applications in optical intra-chip interconnects.

4 Reverse biased PS LEDs for microdisplay applications

After efficient visible photoluminescence has been discovered in porous silicon [4], this material is considered as a candidate for display technologies. Such devices can be fabricated on silicon substrates that are especially attractive for microdisplay technologies. The advantages of porous silicon LEDs for microdisplay application are the following: i) possible integration of driver IC with a PS microdisplay on the same silicon substrate; ii) high resolution of such microdisplay devices due to a minimal size of a light emitting pixel can be few microns; iii) low cost and simplicity of PS fabrication.

The main disadvantage of such LEDs is low efficiency. Taking into account the achieved quantum efficiency of about 1 % (or power efficiency of about 0.3 %) the calculated heat dissipation at light emission from PS LEDs with brightness 100 Cd/m^2 is about 0.3 W/cm^2 . It is obvious that in this case the heat should be removed to prevent overheating effects. However, if the light emission brightness is limited at the level of 20 Cd/m^2 (a usual level for head mounted microdisplay devices operated in the dark), the heat dissipation will not result in catastrophic overheating effects. Such PS microdisplay devices can operate in the continuous regime more than 1000 h without any considerable degradation [22].

Particular attention has been given to the resolution of PS microdisplay devices. Such microdisplays can contain more than a million pixels over the area of 1 cm^2 that cannot be achieved by other existing microdisplay technologies. In this case, the operating current for a pixel is about $10 \mu\text{A}$, which corresponds to the operating current of silicon VLSI components.

Depending on PS anodizing regimes the emission peak can be both in the blue and red range [4]. But all emission spectra are broad enough. Sometimes the spectra cover the whole visible range [21]. Of course, such light emission is suitable for black and white displays, but for a color display other approaches are to be used to get a narrow light emission spectrum. The simplest approach is the employment of light filter. An alternative method of providing a narrow light emission spectrum reported recently in [20,24] is the integration of PS LED with PS microresonator. Thus, PS LEDs can solve miniaturization problems for microdisplay technologies. To improve the operating parameters of the PS LEDs, the work on the optimization of their design and technology is underway.

5 Conclusion

The analysis of reverse biased PS LED developments for the last ten years has shown considerable parameter improvement towards practical implementations of these devices in optoelectronics. The only unresolved problem is insufficient LED efficiency. Nevertheless, the achieved efficiency level of about 1 % allows us consider some special applications. In particular, reverse biased PS LEDs could be

used for optical intra-chip interconnects. The fabricated prototype of optoelectronic unit based on these LEDs has demonstrated the possibility of using photons for communications inside silicon chips. Also the attained LED efficiency is close to the value corresponding to the required level for microdisplay devices. In this case, the high resolution could be afforded that could not be attained by other methods. The development of reverse biased PS LEDs allows us to continue consideration of these devices as candidates for Si based optoelectronics in the near future.

6 Acknowledgements

This work is supported by EC within INCO-COPERNICUS, project 977037, as well as by the Information Fund of Belarus and by the National Basic Research Foundation.

The author would like to thank Professor V. Borisenko for fruitful discussions. The hard work of the group members has permitted to reach the results presented in this paper: P. Jaguiro, A. Leshok, S. Katsouba are gratefully thanked.

References

1. Richter A., Steiner P., Kozlowski F., Lang W., *IEEE Elec. Dev. Lett.* **12** (1991) 691.
2. Lazarouk S., Jaguiro P., Katsouba S., Masini G., La Monica S., Maiello G., Ferrari A., *Appl. Phys. Lett.* **68** (1996) 2108.
3. Gelloz B., Koshida N., *J. Appl. Phys.* **88** (2000) 4319.
4. Cullis A. G., Canham L. T., Calcott P. D. J. *J. Appl. Phys.* **82** (1997) 909; Canham L. T., *Properties of Porous Silicon* (INSPEC, The Institution of Electrical Engineers, London, 1997); Bisi O., Ossicini S., Pavesi L., *Surf. Sci. Rep.* **264** (2000) 1.
5. Kozlowski F., Sauter M., Steiner P., Richter A., Sandmaier H., Lang W., *Thin Solid Films* **222** (1992) 196.
6. Kozlowski F., Steiner P., Lang W., *Proc. NATO ARW Series E: Applied Sciences* **244** (1993) 123.
7. Bertolotti M., Carassiti F., Fazio E., Ferrari A., La Monica S., Lazarouk S., Liakhou G., Maiello G., Proverbio E., Schirone L., *Thin Solid Films* **255** (1995) 152.
8. Searson P. C., Zhang X. G., *J. Electrochem. Soc.* **137** (1990) 2539.
9. La Monica S., Maiello G., Ferrari A., Masini G., Lazarouk S., Jaguiro P., Katsouba S., *Thin Solid Films* **297** (1997) 261.
10. Kuznetsov V., Andrienko I., Haneman D., *Appl. Phys. Lett.* **72** (1998) 3323.
11. Gelloz B., Nakagawa T., Koshida N., *Appl. Phys. Lett.* **73** (1998) 2021.
12. Sze S. M. *Semiconductor Devices: Physics and Technology* (A Wiley-Interscience publication, New York, 1985).

13. Lazarouk S., Bondarenko V., La Monica S., Maiello G., Masini G., Pershukovich P., Ferrari A., *Thin Solid Films* **276** (1996) 296.
14. Toyama T., Matsui T., Kurokawa Y., Okamoto H., Hamakawa Y., *Appl. Phys. Lett.* **69** (1996) 1261.
15. Sercel P., Kwon D., Vilbrandt T., Yang W., Hautala J., Cohen J., Lee H., *Appl. Phys. Lett.* **68** (1996) 684.
16. Lazarouk S. In *Proc. of the 7-th International Symposium Advanced Display Technologies* (Minsk, Belarus, 1998).
17. La Monica S., Balucani M., Lazarouk S., Maiello G., Masini G., Jaguiro P., Ferrari A., *Solid State Phenomena* **54** (1997) 21.
18. Balucani M., La Monica S., Lazarouk S., Maiello G., Masini G., Ferrari A., *Solid State Phenomena* **54** (1997) 8.
19. Lazarouk S. K., Jaguiro P. V., Leshok A. A., Borisenko V. E. In *Physics, Chemistry and Application of Nanostructures* (World Scientific, Singapore, 1999) 370.
20. Lazarouk S. K., Leshok A. A., Borisenko V. E., Mazzoleni C., Pavesi L., *Microelectronic Eng.* **50** (2000) 81.
21. Lazarouk S., Katsouba S., Tomlinson A., Benedetti S., Mazzoleni C., Mulloni V., Mariotto G., Pavesi L., *Mater. Sci. Eng. B* **69/70** (2000) 114.
22. Lazarouk S. K., Jaguiro P. V., Melnikov S. M., Prohorenko A. P., *Izvestia Belorusskoi Injenernoi Akademii* **9** (2000) 67 (in Russian).
23. Cox T. I., Simons A. J., Loni A., Calcott P. D. J., Canham L. T., Uren M. J., Nash K. J., *J. Appl. Phys.* **86** (1999) 2764.
24. Pavesi L., *Riv. Nuovo Cim.* **20** (1997) 1.

ENERGY TRANSFER AND LASING IN InGaN/GaN MULTIPLE QUANTUM WELL HETEROSTRUCTURES

G. P. YABLONSKII, A. V. MUDRYI, E. V. LUTSENKO, V. N. PAVLOVSKII,
I. P. MARKO, V. Z. ZUBIALEVICH

*Stepanov Institute of Physics, National Academy of Sciences of Belarus
F. Skaryna Ave. 68, 220072 Minsk, Belarus*

E-mail: yablon@dragon.bas-net.by

B. SCHINELLER, H. PROTZMANN, M. LUENENBUERGER, M. HEUKEN

*AIXTRON AG
Kackertstr. 15-17, D-52072 Aachen, Germany*

E-mail: bschi@aixtron.com

Energy transfer processes in the InGaN/GaN multiple quantum well (MQW) laser heterostructures are studied using photoluminescence (PL), photoluminescence excitation (PLE) and laser spectroscopy in a wide interval of temperatures (4.2-300 K) and excitation intensities (0.01–1 MW/cm²). It was shown that there are two efficient channels of the energy transfer to the states localized inside the InGaN active layers of both types of the MQWs lasing in the violet (400-440 nm) and in the blue (450-470 nm) spectral regions.

1 Introduction

InGaN/GaN MQW heterostructures are widely used now for display and lighting applications in the spectral range from green to UV. The commercial violet GaN based lasers operating at the emission wavelengths between 390 and 420 nm are available [1]. The real blue InGaN-based lighting displays (LDs) with an emission wavelength near 450 nm were reported only recently [2]. In the course of development of new long wavelength laser structures, investigation of their optical properties is one of the effective methods for layer quality characterization and elucidation of the optimal growth conditions and structure design. Energy transfer processes influence on the laser properties of the MQW structures. Understanding of energy transfer mechanisms using PL and PLE spectroscopy [3] can help to comprehend recombination and gain mechanisms in MQWs.

2 Experimental and results

All samples were grown in an AIX 2000 G3 HT Multiwafer Planetary Reactor[®] in the 6 x 2 inch configuration using TMGa, TEGa, TMI_n and NH₃ as precursors. On the top of 1-4 μm thick GaN or GaN/GaN:Si buffer layers a 10 period MQW stack was grown under different growth conditions. The MQWs differ in thickness and in

content of the active layers. The lasers based on structures with the active layer of 4-10 nm (MQW1-1 and MQW1-2) showed laser action at optical excitation in the violet region of 400–440 nm [4]. The lasers (MQW2-1 and MQW2-2) with the active layer of 1.9–2.4 nm had the operative wavelength in the blue spectral region 450–470 nm.

PL and stimulated emission spectra from InGaN/GaN MQW heterostructures were investigated as a function of excitation intensity (I_{exc}) of the N_2 laser radiation ($h\nu = 3.68$ eV, $f = 1000$ Hz, $t = 8$ ns, $I_{\text{exc}} = (0.01\text{--}1)$ MW/cm²) in the temperature range 78–300 K. The PL and PLE spectra were measured at 4.2 K, 78 K and 300 K under excitation by quasi-monochromatic light dispersed from a xenon lamp by a monochromator.

Fig. 1 and 2 show PL and PLE spectra of the both series of InGaN/GaN MQW heterostructures measured at 4.2 K. The PL spectra of all samples consist of a low intensity line near 3.5 eV belonging to emission from the GaN barrier layers and an intensive broad band from the active layers located between 2.4 eV and 2.8 eV. The PLE spectra of the emission from QW layers reveal an UV band due to the light absorption in the GaN barrier layers and a low energy band near the mobility edge of the active layer.

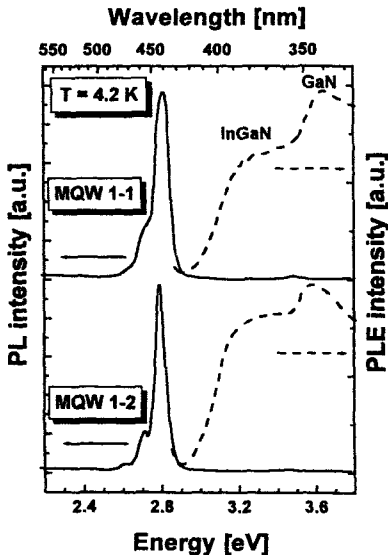


Figure 1. Normalized PL (solid) and PLE (dashed) spectra of InGaN/GaN quantum well structures MQW1-1 and MQW1-2 at 4.2 K.

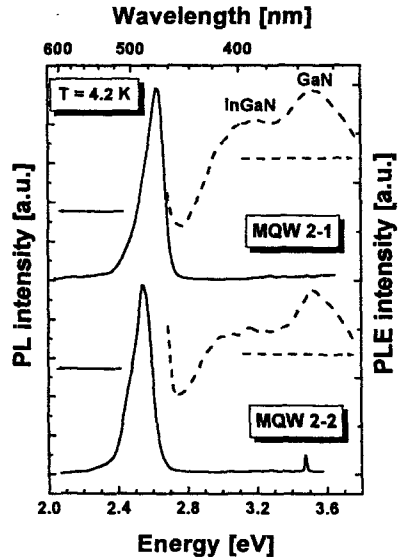


Figure 2. Normalized PL (solid) and PLE (dashed) spectra of InGaN/GaN quantum well structures MQW2-1 and MQW2-2 at 4.2 K.

The PL and PLE spectra demonstrate the high Stokes shift between the luminescence and absorption. This means that the radiative recombination at low

excitation intensity is due to the In-rich clusters inside the quantum well layers like quantum dots or quantum discs. The energy transfer into the localized states is attributed to the nonequilibrium carrier diffusion from the GaN barriers to the InGaN active layers followed by their trapping at the localized states for the case of UV exciting light. The second mechanism of the energy transfer is a direct excitation of the carriers with energy near the mobility edge of the InGaN layers. A high efficiency of the last mechanism is an evidence of the active layer good quality. The PLE and PL spectra of the both types of heterostructures at the higher temperatures $T=78\text{ K}$ and $T=300\text{ K}$ share approximately the same properties: a large Stokes shift and two channels of the energy transfer.

The PL and PLE bands of the “blue” laser structures (MQW2) are shifted to the low energy range comparing to that of the “violet” laser structures (MQW1). It evidences on the higher In concentration in the MQW2 structures and explains the longer wavelengths of the lasers based on the MQW2 heterostructures. Fig. 3 exhibits the PL and laser spectra of both types of structures at 300 K under different excitation intensities of the pulsed laser radiation. The PL spectra of the MQW1-1 demonstrate a large shift of the emission band to the high energy side with increasing I_{exc} . At the same time, the PL spectra of the MQW2-2 do not show any significant shift, but stimulated emission bands appear at relatively low I_{exc} .

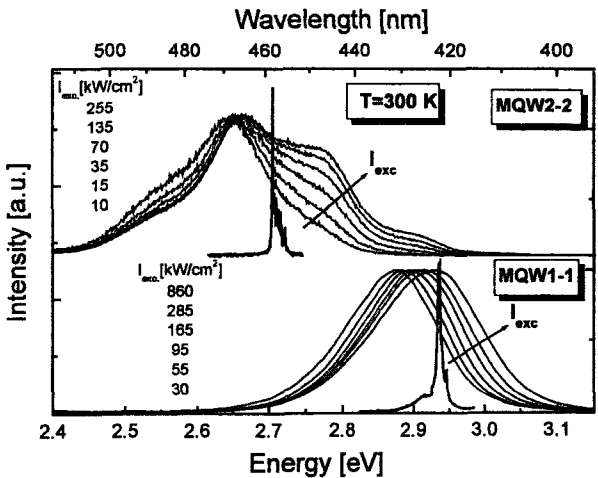


Figure 3. Room temperature PL and laser (narrow) spectra of the samples MQW2-2 and MQW1-1 under different excitation intensities.

The difference in the PL spectra structure of the both samples evidences on difference in recombination and gain mechanisms in the MQWs which needs further examination. The laser thresholds of the long wavelength laser structures

was 2-3 times higher than that of the short wavelength lasers despite the first structures had the higher PL efficiency and the lower PL band widths. The difference in the laser thresholds may be explained by the lower optical confinement factor of the long wavelength lasers attributed to the small thickness of their active layers.

3 Summary and conclusions

PL and PLE spectra of the two series of InGaN/GaN MQW heterostructures were investigated in the temperature range from 4.2 K to 300 K to understand the energy transfer mechanisms. It was shown that there are two efficient channels of the energy transfer to the states localized inside the InGaN active layers of both types of the MQWs lasing in violet and blue spectral regions. The higher laser threshold value of the "blue" lasers is due to the smaller active layer thickness and the lower optical confinement factor comparing to the "violet" lasers.

4 Acknowledgements

The work was partly supported by the ISTC project B-176.

References

1. Nakamura S., Senoh M., Nagahama S., Matsushita T., Kiyoku H., Sugimoto Y., Kozaki T., Umemoto H., Sano M., Mukai T., Violet InGaN/GaN/AlGaIn based laser diodes operable at 50°C with a fundamental transverse mode, *Jpn. J. Appl. Phys.* **38** (1999) pp L226-L229.
2. Nakamura S., Senoh M., Nagahama S., Iwasa N., Matsushita T., Mukai T., Blue InGaIn-based diodes with an emission wavelength of 450 nm, *Appl. Phys. Lett.* **76** (2000) pp 22-24.
3. Schmidt T. J., Cho Y.-H., Gainer G. H., Song J. J., Keller S., Mishra U. K., DenBaars S. P., Pump-probe spectroscopy of band tail states in MOCVD-grown InGaIn, *Appl. Phys. Lett.* **73** (1998) pp. 1892-1894.
4. Marko I. P., Lutsenko E. V., Pavlovskii V. N., Yablonskii G. P., Schön O., Protzmann H., Lünenbürger M., Schineller B., Heime K., High-temperature lasing in InGaIn/GaN multiquantum well heterostructures, *Phys. Stat. Sol. (b)* **216** (1999) pp. 491-494.

A NEW MULTYPEAK RESONANT TUNNELING DIODE FOR SIGNAL PROCESSING APPLICATION

A. N. KHOLOD¹, M. LINIGER², A. ZASLAVSKY³, A. L. DANILYUK⁴,
F. ARNAUD D'AVITAYA¹

¹ *Centre de Recherche sur les Mécanismes de la Croissance Cristalline
Campus de Luminy - Case 913, 13288 Marseille cedex 9, France*

² *Biel School of Engineering and Architecture
2501 Biel, Switzerland*

³ *Division of Engineering, Brown University
Providence, Rhode Island 02912, USA*

⁴ *Belarusian State University of Informatics and Radioelectronics
P. Browka 6, 220013 Minsk, Belarus*

E-mail: kholod@crmc2.univ-mrs.fr

A novel design of cascaded resonant tunneling device is proposed and theoretically described. It consists of diodes with linearly increasing area connected in series. There are with separate contacts to interconnecting doped layers between the diodes. The device is shown to have a predictable successive diode quenching as well as an allowance for differential voltage measurements detecting this quenching. These features are useful to perform an analog-to-digital signal conversion.

1 Introduction

There has been a wide range of experimental and theoretical work on resonant tunneling of charge carriers in solid state structures, especially since the devices based on this phenomenon can be made to exhibit negative differential resistance in their current-voltage (I - V) characteristics. This effect is explored for functional devices in different circuit applications [1]. Moreover, greatly reduced circuit complexity can be realized using the resonant tunneling devices with multiple negative resistance regions [2]. They are produced from the ground-state resonances of several vertically integrated resonant tunneling diodes in cascade [3]. By varying the thickness of the barrier and the spacer layers, one can tailor the peak-to-peak voltage, the peak-to-valley ratio, and the peak current of such a device to match the application needs. Analog-to-digital converters taking advantage of such multipeak resonant tunneling I - V characteristic have been reported on so far [4,5]. However, their architecture has not been designed to perform a flash (parallel) operation.

In this work we have attempted to include new features into the design of cascaded resonant tunneling diodes in order to achieve a flash analog-to-digital signal processing. It is suggested to connect in series the diodes of linearly increasing area and to have contacts to each interconnecting doped layers between

the diodes. The simulations of the device I - V characteristic as well as its functioning as a converter have been carried out and are presented in the paper.

2 Structure design and modeling

The schematic representation of the cascaded resonant tunneling structure we propose is given in Fig. 1(a). It consists of $N = 7$ double barrier resonant tunneling diodes decoupled through a highly doped connecting layers. These layers are assumed to be thick enough (50-100 nm) to consider the transfer of electrons across different resonant tunneling diodes as the sequence of incoherent events and also to allow for a low-access-resistance output terminal in-between the diodes. The main characteristic feature of the device is that the size of the active area for each resonant tunneling diode in the series increases linearly. An equivalent circuit of the structure is shown in Fig. 1(b). It includes a series of $N = 7$ sub-circuits, each consisting of a nonlinear resistor and a capacitor in parallel (the small series resistance of the doped layers between the resonant tunneling diodes is ignored). A physical reason for an equivalent description chosen for one resonant tunneling diode is very clear. A resonant tunneling junction presents a resistance for a dc current, and if tunneling can be neglected the junction is equivalent to a capacitor. Such a representation was already used in the past for description of current instabilities and the formation of high-field domain in superlattices [6].

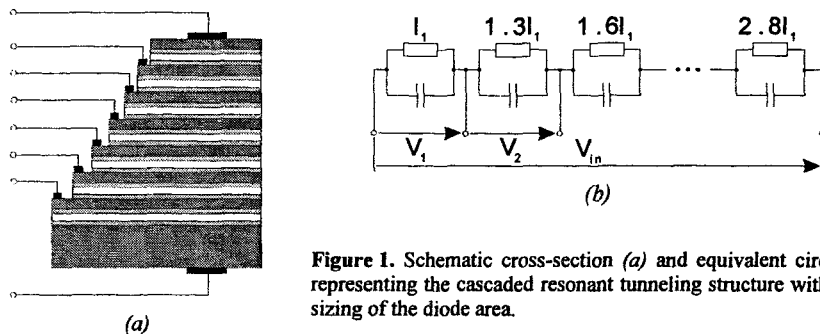


Figure 1. Schematic cross-section (a) and equivalent circuit (b) representing the cascaded resonant tunneling structure with linear sizing of the diode area.

The dynamics of the circuit shown in Fig. 1(b) is described by the following system of equations

$$C_i \frac{dV_i}{dt} + J_i(V_i) = I, \quad i = 1, 2, \dots, N,$$

$$\sum_{i=1}^N V_i = V_{in},$$

where V_i is the voltage drop across the i -th diode; V_{in} is the input voltage; $J_i(V_i)$ is the I - V response from the i -th diode; I is the current passing through the device; C_i is the capacitance of the i -th diode. To model the I - V characteristics of the device we have assumed that an individual double-barrier resonant tunneling diode provides an I - V characteristic with a current peak at a source-drain bias $V_p = 0.2$ V,

a peak-to-valley ratio of 10, and a smooth transition through the valley current region. Clearly, increasing the resonant tunneling diode area simply changes the peak current proportionally. These I - V curves have been taken into our model as functions $J_i(V_i)$. However, we would like to argue that our results do not depend qualitatively on the exact shape of the curves.

3 Results

The simulated I - V characteristics of the cascaded resonant tunneling structure is presented in Fig. 2. There are 7 regularly spaced current peaks with successively increased amplitudes. The operation is not at all different from a cascaded resonant tunneling structure with N identical diodes in series [3] and is similar to the effect observed in superlattices [7]. In ideal case, when the cascade structure combines identical resonant tunneling diodes, the physics of operation consists in propagation of high-field domain from anode towards the cathode causing thereby the sequential quenching of the resonant tunneling diodes. The process is governed by the self-consistent dynamical space-charge buildup due to tunneling carriers. However, in real life there is always some dispersion in the epitaxial and geometrical parameters of the nominally identical resonant tunneling diodes, leading to unpredictable switching order determined by the scatter in the peak current of individual diodes [8]. The central idea of our device is to control diode switching by progressively changing the resonant tunneling diode area. Hence, the successive increase in the current peak amplitude of our device reflects the order in which the diodes switch.

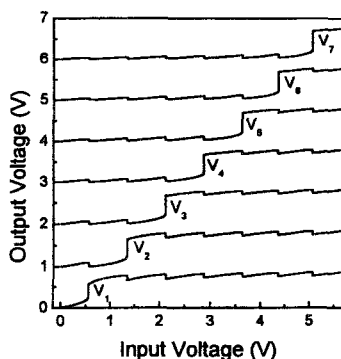
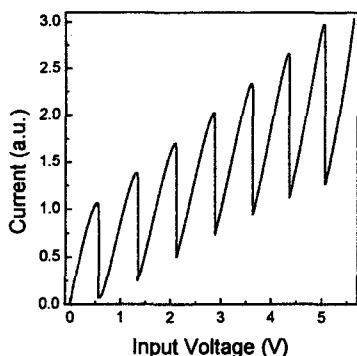


Figure 2. Simulated I - V characteristic of the cascaded ($N=7$) resonant tunneling structure with linearly changing diode area.

Figure 3. Simulated transfer curves of the 7-bit quantizer based on the cascaded ($N=7$) resonant tunneling structure with linearly changing diode area.

To achieve the quantizer function, required for any analog-to-digital signal conversion, one simply needs to take the differential voltage measurements across the resonant tunneling diodes at the output terminals (Fig. 1(b)). In this case, the

transfer curves for 7 digital outputs are demonstrated in Fig. 3. They are shifted for clarity. For a given input voltage V_{in} the structure is broken down in two part regarding the voltage distribution along it. Therefore, the differential voltage exists in two possible states: if a given resonant tunneling diode has switched, the voltage across it is high (~ 0.75 V, given our I - V resonant tunneling diode characteristic); if it has not, the voltage is low ($< V_p \sim 0.2$ V). The transition from low state to high state is steep and the separation between these two voltage regimes is evident.

According to the above the device outputs an 8-level (7-bit) thermometer code demonstrating thereby the ability of the cascaded resonant tunneling structure proposed to function as a quantizer. One can see that to achieve N -bit resolution for thermometer code, N resonant tunneling diodes should be integrated in one structure. Clearly, in order to have a binary coded word an additional encoding scheme is required.

4 Conclusion

A simple concept for analog-to-digital flash conversion performed by a series connection of resonant tunneling diodes with linearly increasing area has been described. A predictable sequence of resonant tunneling diode switching is achieved. Differential voltage measurements between the output electrodes at the source and drain of each resonant tunneling diode produce high and low voltage values corresponding to digital zero and one states. The resulting flash quantizer could reduce the circuit complexity for high-speed analog-to-digital signal processing.

Acknowledgments

We would like to thank S. Luryi and V. E. Borisenko for fruitful discussions of the obtained results.

References

1. Capasso F., Sen S., Beltram F., Lunardi L. M., Vengurlekar A. S., Smith P. R., Shan N. J., Malik R. J., Cho A. Y., Quantum functional devices: resonant-tunneling transistors, circuits with reduced complexity and multiple-valued logic, *IEEE Trans. Electron Devices* **36** (1989) pp. 2065-2082.
2. Sen S., Capasso F., Cho A. Y., Sivco D., Resonant tunneling device with multiple negative differential resistance: digital and signal processing applications with reduced circuit complexity, *IEEE Trans. Electron Devices* **ED-34** (1987) pp. 2185-2191.

3. Sen S., Capasso F., Sivco D., Cho A. Y., New resonant-tunneling devices with multiple negative resistance regions and high room-temperature peak-to-valley ratio, *IEEE Electron Device Lett.* **9** (1988) pp. 402-404.
4. Kuo T. H., Lin H. C., Potter R. C., Shupe D., A novel A/D converter using resonant tunneling diodes, *IEEE J. Solid-State Circuits* **26** (1991) pp. 145-149.
5. Wei S.-J., Lin H. C., Potter R. C., Shupe D., A self-latching A/D converter using resonant tunneling diodes, *IEEE J. Solid-State Circuits* **28** (1993) pp. 697-700.
6. Laikhtman B., Current-voltage instabilities in superlattices, *Phys. Rev. B* **44** (1991) pp. 11260-11265.
7. Kholod A. N., Borisenko V. E., Zaslavsky A., Arnaud d'Avitaya F., Current oscillations in semiconductor-insulator multiquantum wells, *Phys. Rev. B* **60** (1999) pp. 15975-15979.
8. Kuo T. H., Lin H. C., Potter R. C., Shupe D., Analysis of the hysteresis in the I - V characteristics of vertically integrated, multi peaked resonant-tunneling diodes, *J. Appl. Phys.* **68** (1990) pp. 2496-2498.

A CYCLOTRON RESONANCE QUANTUM HALL EFFECT DETECTOR

B. A. ANDREEV, I. V. EROFEEVA, V. I. GAVRILENKO, A. L. KOROTKOV,
A. N. YABLONSKIY

*Institute for Physics of Microstructures of Russian Academy of Sciences
GSP-105, 603600 Nizhny Novgorod, Russia*

E-mail: gavr@ipm.sci-nnov.ru

O. ASTAFIEV, Y. KAWANO, R. S. KOMIYAMA

*Department of Basic Science, The University of Tokyo
Komaba 3-8-1, Meguro-ku Tokyo 153, Japan*

E-mail: csusumu@ASone.c.u-tokyo.ac.jp

Far infrared photoresponse of the QHE device operating at cyclotron resonance has been investigated. The possibility of the detector band tuning at the simultaneous increase of the magnetic field and the 2D electron concentration (due to the persistent photoconductivity after band-gap illumination) is demonstrated. Time characteristics of the response have been studied.

1 Introduction

Far infrared (FIR) photoresponse of high mobility two-dimensional (2D) electrons in GaAs/AlGaAs heterostructures under cyclotron resonance (CR) has been the subject of several studies (see, for example [1,2]). In high magnetic fields when the Fermi level E_F lies in localized states between two adjacent Landau levels the Hall resistance is quantized and the longitudinal resistance R_{xx} vanishes. The finite R_{xx} emerges when electrons and holes are photoexcited in delocalized states near the level centers above and below E_F . Therefore, quantum Hall effect (QHE) devices may serve as an excellent CR detector in FIR range. In the present work the possibility of the detector tuning as well as its time characteristics were investigated.

2 Experimental

The detector was fabricated from the GaAs/Al_{0.3}Ga_{0.7}As heterostructure with high mobility ($\mu_{4.2K} = 8 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$) 2D electron gas. It was a Hall bar of 170 mm in length and 50 μm in width patterned in zig-zag shape and fitted into an area $4 \times 4 \text{ mm}^2$ [1]. The sample placed in liquid helium at in the center of superconducting solenoid was biased by DC current of 3 μA . FIR radiation was guided to the sample

by stainless steel light pipe. Black body source ($T = 600^\circ\text{C}$) was used to reveal the detector sensitivity bands over magnetic fields (up to 6T). The spectral study was carried out using a BOMEM DA3.36 FT spectrometer. The tuning of the detector band was provided by the simultaneous increase of the magnetic field (and correspondingly CR frequency) and the concentration of 2D electrons by illumination of the sample by radiation ($\lambda \approx 0.9\ \mu\text{m}$) of GaAs light emitting diode (LED). The increase of the carrier concentration resulted from the illumination persists after the LED switching off up to the thermal recycling of the sample (persistent photoconductivity effect [3]). Time characteristics of the detector response were studied using broad band FIR emission of hot holes in InGaAs/GaAs multiple-quantum-well heterostructure ([4]) excited by pulsed lateral electric field (about 10 μs in duration).

3 Results and discussion

Magnetic field dependences of longitudinal resistance R_{xx} and photoresponse on the broad band black body source radiation of QHE device are shown in Fig. 1. 2D electron concentration obtained from the period of Shubnikov-de Haas (SdH) oscillations is $2.8 \times 10^{11}\ \text{cm}^{-2}$. It is clearly seen that the response occurs near R_{xx} minima, i.e. at the even values of Landau level filling factor $\nu = 2, 4, 6, 8, 10$, etc. Spectral investigation of the response shows that it consists of sharp CR line with full width at half maximum (FWHM) of 2 to 3 cm^{-1} ($m_e \approx 0.068\ m_0$, cf.[5]). The absolute measurements of the response at $\nu = 4$ and $\nu = 6$ gave the same value $S_V \approx 10^4\ \text{V/W}$ at $\text{NEP} \approx 10^{-11}\ \text{W/Hz}^{1/2}$ that is comparable with the existing semiconductor photoelectric detectors.

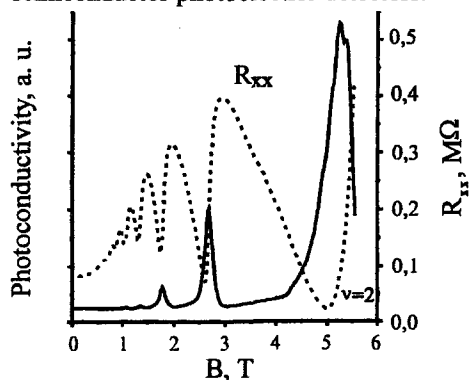


Figure 1. Longitudinal resistance R_{xx} and photoresponse on the black body radiation of QHE device versus the magnetic field.

At the sample illumination by LED radiation R_{xx} minima shift to the higher magnetic fields. This is a result of the increase of 2D electron concentration due to the persistent photoconductivity effect. The maximum shift reaches 80 % that opens the possibility of continuous tuning of the detector sensitivity band. The tuning is illustrated in Fig. 2 where the photoresponse spectra measured at the magnetic fields near R_{xx} minimum ($\nu = 6$) are presented. It is clearly seen that the photoresponse consists of the narrow CR line. By

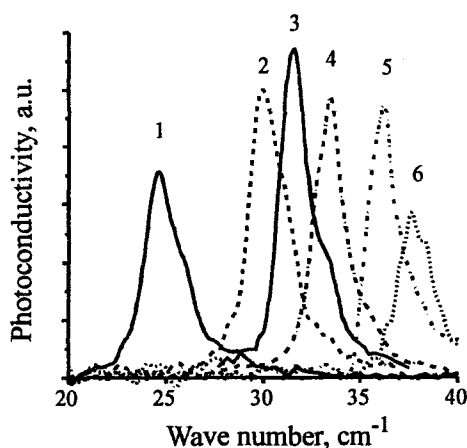


Figure 2. Photoresponse spectra measured at magnetic fields near the R_{xx} minimum at $\nu=6$. Spectra 1 to 6 correspond to increasing numbers of LED radiation pulses of 500 μ s in duration.

voltage is switched off is much longer, about 200 μ s. Such behavior can be naturally explained by arising fields of localized states between the centers of the Landau levels in high magnetic field, which are responsible for QHE. A considerable part of electrons and holes generated by the FIR radiation above and under the Fermi level, respectively, seems to fall into minima (electrons) and maxima (holes) of long range disordered potential responsible for the existence of the localized states. Owing to the energy exchange among the photoexcited carriers and to the interaction with the acoustical phonons, a localized electron (hole) can be excited occasionally to a delocalized state formed around the Landau level center (and thus to participate in DC conductivity), then re-captured by the localized state, excited once again, etc. The time constant of the detector response is, therefore, the recombination lifetime of the excited carrier. Since the excited electron and hole captured by localized states are spatially separated, the lifetime is strongly (exponentially!) affected by the overlapping of their wavefunctions. In high magnetic fields the scale of wavefunction extension is the magnetic length that is decreased with the field, thus resulting in a marked increase of the detector response time at $\nu=2$ if compared with the cases $\nu=6$ and $\nu=4$.

4 Acknowledgements

This work was financially supported by RFBR (Grants #00-02-16568, #00-02-81022), Russian Scientific Programs "Physics of Solid State Nanostructures" (#99-1128), "Physics of Microwave" (#4.5), "Fundamental Spectroscopy" (#8/02.08),

simultaneous increasing of illumination and the magnetic field the line is tuned to higher frequencies, with approximately the same FWHM. Such tuning demonstrates the possibility to utilize QHE detector as spectral analyzer for the FIR range.

Another important feature of the detector is its response time. Operating at the magnetic fields corresponding to the filling factor $\nu=6$ and $\nu=4$, the detector exhibits a rather fast response ($\tau \leq 5 \mu$ s). At the same time, at higher magnetic fields at $\nu=2$ the response time determined from the response decay after the emitter

"Leading Scientific Schools" (#00-15-96618), "Integration" (##540, 541) and "The Universities of Russia" (#015.01.01.94).

References

1. Komiyama S., Kawano Y., Hisanaga Y., Quantum Hall devices as a tunable and high sensitive FIR detector. In *Proc. of 21st Int. Conf. Infrared and Millimeter Waves*, ed. by M. von Ortenberg, H.-U. Mueller (Humboldt University, Berlin, 1996) BT2.
2. Stein D., Ebert G., von Klitzing K., Weimann G., Photoconductivity on GaAs-Al_xGa_{1-x}As heterostructures, *Surf. Sci.* **142** (1984) pp. 406-411.
3. Störmer H. L., Gossard A. C., Wiegmann W., Baldwin K., Dependence of electron mobility in modulation-doped GaAs-(AlGa)As heterojunction interfaces on electron density and Al concentration, *Appl. Phys. Lett.* **39** (1981) pp. 912-914.
4. Aleshkin V. Ya., Andronov A. A., Antonov A. V. et al., Infrared radiation from hot holes during spatial transport in selectively doped InGaAs/GaAs heterostructures with quantum wells, *JETP Lett.* **64** (1996) pp. 520-524.
5. Antonov A. V., Erofeeva I. V., Gavrilenko V. I. et al., Spectral response of cyclotron resonance quantum Hall effect detector. In *Inst. Phys. Conf. Ser. No 162*, ed. by H. Sakaki et al. (Institute of Physics, Bristol, 1999) pp. 111-116.

THE ROLE OF SHALLOW AND DEEP TRAPS IN CARRIER TRANSPORT ACROSS SILICON/INSULATOR NANOSTRUCTURES

J. A. BERASHEVICH, A. L. DANILYUK

Belarusian State University of Informatics and Radioelectronics

P. Browka 6, 220013 Minsk, Belarus

E-mail: julia@nano.bsuir.edu.by

Effect of trap energy levels on carrier transport across nanosize structures Si/CaF₂ is considered. The charge accumulated by these traps and subsequent discharge of the traps are found to result in the shift of the current origin as well as in the appearance of negative differential resistance region on current-voltage characteristics. Deep and shallow traps are observed to control the transport phenomena at high and low temperatures, respectively.

1 Introduction

Nanosize structures containing multiquantum wells have attracted attention of many researches because of the perspective to fabricate solid-state devices for nanoelectronics [1]. Silicon/insulator structures seem to be very promising due to the compatibility with good elaborated silicon technology.

In the previous study of carrier transport across Si/CaF₂ quantum wells (QWs) [2,3], carrier transfer through deep trap levels in the insulator was found to influence dramatically current-voltage (I - V) characteristics of these structures. However, the experimental investigations give an evidence that dielectric layers can contain both deep and shallow trap levels [2]. The deep levels have an activation energy from 0.6 to 0.8 eV, while levels from 0.3 to 0.45 eV belong to the shallow traps. The role of the two trap levels in the carrier transport across nanostructures has not been clearly established.

In this paper, we present results of theoretical simulation of carrier transport across silicon/insulator nanosize structures containing traps with different energy levels.

2 Model

The periodical structure considered consists of Si and CaF₂ layers forming a system of quantum wells and potential barriers. The kinetic model for charge carrier transfer across such structure has been developed elsewhere [3,4]. In this work it is assumed that electrons and holes carry the charge via direct tunneling across the potential barriers as well as via traps in the dielectric layers. The thermoactivating capture of the carriers by the traps with their subsequent release by the relay rally

way have been shown to dominate in the carrier transport across QWs [4]. This results in charge accumulation in the dielectric. To model the influence of the shallow and deep traps on I - V characteristics of the structures we choose their energy levels to be 0.3 and 0.6 eV, respectively, as they were observed experimentally [2]. The system of transport equations used for simulation was the same like in [4].

3 Results and discussion

Calculated I - V characteristics of the 6-period Si/CaF₂ structure containing shallow and deep trap levels are shown in Fig. 1 for different absolute temperatures. An interesting feature we want to stress is the current shift on the I - V curves. The “zero” current point is shifted towards negative voltages. Moreover, the largest

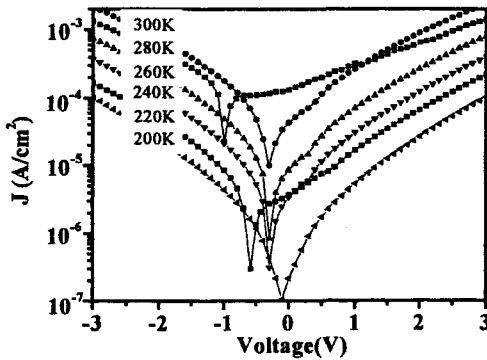


Figure 1. I - V characteristics of the 6-periods Si/CaF₂ structure at different temperatures.

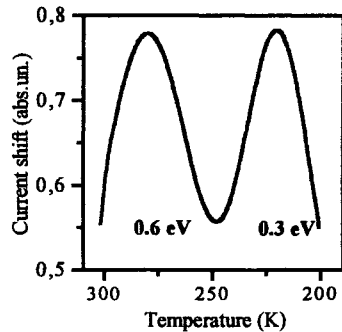


Figure 2. The shift of the current origin as a function of temperature and energy position of the taps.

shift of the current origin appears at 280 and 220 K. In our previous work [4] it was shown that the phenomena observed related to charging and discharging processes. When the bias is applied, the traps start to capture the carriers and as the capture time can be of the order of the voltage step delay time, the charge is accumulated in the dielectric. Polarization of this charge by the external bias causes an appearance of the internal electric field in the structure and results in the “zero” current shift in I - V characteristics.

The degree of the dielectric polarization depends on the quantity of the free trap states. There should be a spatial separation of captured electrons and holes. The maximum effect is reached when the trap states are half-filled. At room temperature the shallow traps are completely occupied, whereas the deep traps are not charged yet. This is directly reflected in the transport across the structure, particularly, in the

“zero” current shift. The temperature dependence of this shift is shown in Fig. 2. The effect of shallow and deep traps appears in the different temperature intervals. Deep traps (0.6 eV) are responsible for the effect at high temperatures, while shallow traps (0.3 eV) control it at low temperatures.

4 Conclusions

Within the kinetic model, the carrier transport across periodic Si/CaF₂ nanostructures containing deep and shallow traps in the dielectric has been investigated. The charge polarization depends on the trap occupation having maximum for half-filled states. This conditions the temperature dependence of the “zero” current shift in the *I-V* characteristics of the structures mediated by the charge polarization.

5 Acknowledgments

The authors are grateful to V. E. Borisenko and A. N. Kholod for initiating this work and fruitful discussions of the results obtained.

References

1. *Resonant Tunneling in Semiconductors*, ed. by L. L. Chang (Plenum, New York, 1996).
2. Ioannou-Sougleridis V., Tsakiri V., Nassiopoulou A. G., Bassani F., Menard S., d'Avitaya F. In *Silicon Modules for Integrated Light Engineering, ESPRIT MEL-ARI project n°28741* (Marseille, 1999) 209.
3. Kholod A. N., Danilyuk A. L., Borisenko V. E., Bassani F., Menard S., d'Avitaya F., *J. Appl. Phys.* **85** (1999) 7219.
4. Berashevich J. A., Danilyuk A. L., Kholod A. N., Borisenko V. E., *Semiconductors* **35** (2001) 112.

LONG TERM CHARGE RELAXATION IN SILICON SINGLE ELECTRON TRANSISTORS

A. SAVIN, A. MANNINEN, P. KIVINEN, J. PEKOLA

*Department of Physics, University of Jyväskylä
P.O.Box 35, FIN-40351, Finland*

M. PRUNNILA, J. AHOPELTO

*VTT Microelectronics Centre
P.O.Box 1101, FIN-02044 VTT, Finland*

M. KAMP, M. EMMERLING, A. FORCHEL

*Technische Physik, Universität Würzburg
Am Hubland, D-97074 Würzburg, Germany*

E-mail: savin@phys.jyu.fi

Silicon single electron transistors with a side gate have been fabricated on a heavily doped silicon-on-insulator substrate. I-V characteristics of all devices have a Coulomb blockade region. Electrical conductivity of single electron transistors demonstrates long term relaxation after cooling to 4.2 K. At temperatures below 20 K long-term relaxation of the source-drain current after switching of the gate voltage has been observed.

1 Introduction

Single electron tunneling devices are considered as perspective devices for future micro- and nanoelectronic circuits. Silicon is very promising material for nanotechnology due to the possibility to utilize standard Si technology and to use oxidation process for the reduction of the final size of the structures. Essential success has been achieved in the development of silicon-based single electron transistors (SETs) operating at rather high temperatures [1,2], logic elements [3] and memory modules [4,5] based on single electron effect. However, a high level of doping and the implantation procedure introduce additional defects that may lead to slow processes due to relaxation of background charge at low temperatures [6,7]. In this paper we report on investigation of side-gated silicon SETs fabricated on a heavily doped thin silicon-on-insulator (SOI) substrate. Some of these results will be published elsewhere [8].

2 Samples

Silicon SETs with side gate have been fabricated on a heavily doped SOI wafer. The wafer was doped by phosphorous implantation (20 keV, $8 \times 10^{14} \text{ cm}^{-2}$) with following oxidation in dry ambient at 1080 °C for 35 min. The large-scale structures of the samples were defined by UV-lithography. Then the mesas were modified by electron beam lithography and dry etched to obtain the SET device structure schematically shown in Fig. 1. Next, the wafer was oxidized, reducing the final dimensions. Electron concentration in the SOI film was about $3 \times 10^{19} \text{ cm}^{-3}$.

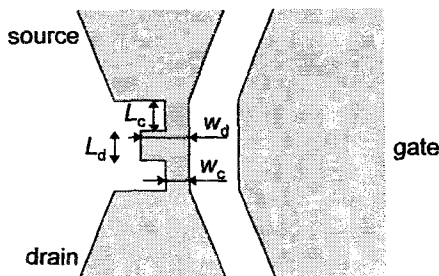


Figure 1. Schematic top view of the SET with a side gate. The dimensions are $L_c = L_d = 100 \text{ nm}$, $w_d = 150 \text{ nm}$, $w_c = 80 \text{ nm}$ and $w_g = 100 \text{ nm}$ for different samples.

3 Results and discussion

3.1 Coulomb blockade and gate modulation

Devices fabricated on the same substrate have different characteristics: SETs demonstrate the multiple dot array behavior at a low temperature and only one sample demonstrates the single island behavior in a wide range of temperatures. I-V characteristics of all SETs under investigation demonstrate the clear Coulomb blockade region at temperatures up to 100 K and the pronounced nonlinear behavior even at 300 K.

Source-drain current (I_{ds}) as a function of gate voltage at $T = 4.2 \text{ K}$ are plotted in Fig. 2(a) for one of the multiple dot devices. The multiple dot samples demonstrate rather complicated modulation of I_{ds} by gate voltage, which may be described by electron tunneling through few dots connecting in series or (and) in parallel. The smallest period of 60-70 mV observed on multiple dot samples corresponds to the gate-dot capacitance about 2.5 aF and dot diameter about 30 nm, that is a reasonable size for a dot which was expected to be formed in the central part of our structure after the final oxidation.

3.2 Relaxation after cooling to 4.2 K

Sometimes after cooling to helium temperature, conductivity of the samples relaxes during long time to its stable value. The conductance of the SET immediately after cooling does not depend on

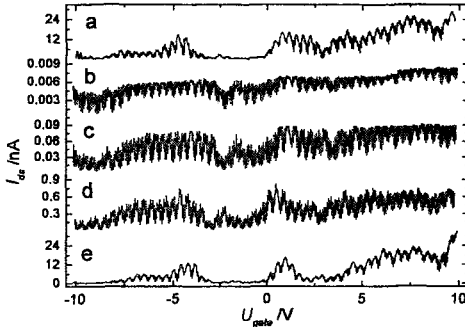


Figure 2. Drain-source current vs. gate voltage at 4.2 K ($U_{ds} = 10$ mV): (a) - before thermal cycling up to 300 K, (b) - after thermal cycling up to 300 K and cooling to 4.2 K, (c) - 30 min after cooling to 4.2 K, (d) - 2 days after cooling to 4.2 K, (e) - 10 days after cooling to 4.2 K.

this relaxation is a charge redistribution in lightly doped p-type silicon substrate, which affects the tunnel resistance of the SET. Similar effect of charge relaxation in the substrate upon properties of single electron devices has been reported previously [6,7].

3.3 Current relaxation (oscillation)

At temperatures below 20 K, the long term oscillations (relaxation) of source-drain current after switching of the gate voltage were observed in both multiple dot and single dot samples. Drain-source current as a function of time is plotted in Fig. 3 at different temperatures. Gate voltage is switched from -12.6 V to +6.6 V at $t = 0$. The switching of the gate voltage at a low temperature is followed by current oscillations. The relaxation process continues for about 20–40 min at 4.2 K. With an increase of the temperature the rate of the process increases (characteristic time decreases) and at $T > 20$ K there is no noticeable relaxation of the drain-source current after switching of the gate voltage. This phenomenon is probably caused by slow relaxation of the background charge. This charge may be associated with surface defects at Si-SiO₂ interface and deep traps in silicon oxide and heavily doped silicon layers. Change of the gate voltage initiates emission and capture processes with corresponding redistribution of the charge that leads to long term relaxation of effective electric field and oscillation of the drain-source current.

cooling does not depend on the cooling rate and is not reproducible in different cooling cycles. The equilibrium state after the relaxation is rather reproducible in all thermal cycles for all samples. During the relaxation, conductivity of the SET can increase by several orders of magnitude (Fig. 2), but there are no noticeable changes in the periods of I_{ds} modulation. Illumination of the sample by the light with characteristic photon energy about 1.9 eV does not affect the relaxation process. A possible origin of

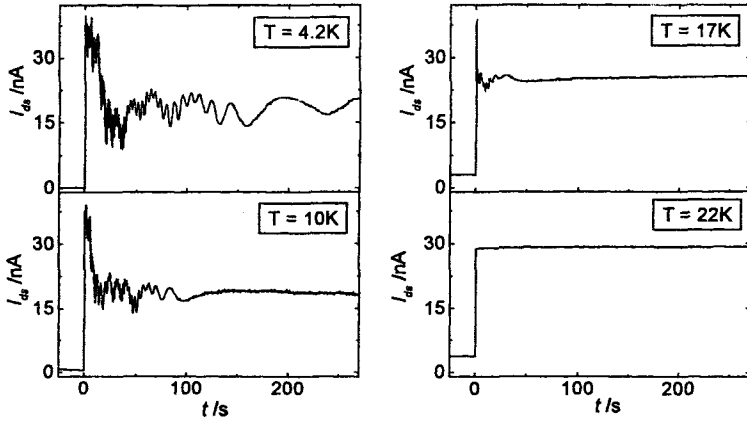


Figure 3. Response of the drain-source current to the step change in the gate voltage U_{gate} at different temperatures. U_{gate} is switched from -12.6 V to +6.6 V at $t = 0$, $U_{ds} = 10$ mV.

Illumination of the SETs by the red light (~ 1.9 eV) suppresses the relaxation process. Charge carriers photo-generated under illumination speed up the charge redistribution processes, resulting in the faster relaxation of the SET current.

4 Acknowledgments

This work has been supported by Vilho, Yrjö and Kalle Väisälä Foundation, and by the Academy of Finland through projects 46804, 46805, and 39081, and by the European Commission through LTR project Q-SWITCH (ESPRIT 30960).

References

1. Zhuang L., Guo L., Chou S., *Appl. Phys. Lett.* **72** (1998) 1205.
2. Ishikuro H., Hiramoto T., *Appl. Phys. Lett.* **71** (1997) 3691.
3. Ono Y., Takahashi Y., Yamazaki K., Nagase M., Namatsu H., Kurihara K., Murase K., *Appl. Phys. Lett.* **76** (2000) 3121.
4. Nakajima A., Futatsugi T., Kosemura K., Fukano T., Yokoyama N., *Appl. Phys. Lett.* **70** (1997) 1742.
5. Irvine A. C., Durrani Z. A. K., Ahmed H., *J. Appl. Phys.* **87** (2000) 8594.
6. Zorin A. B., Ahlers F.-J., Niemeyer J., Weimann T., Wolf H., Krupenin V. A., Lotkhov S. V., *Phys. Rev. B* **53** (1996) 13682.
7. Martinis J. M., Nahum M., *Phys. Rev. Lett.* **72** (1994) 904.
8. Manninen A., Kauranen J., Pekola J., Savin A., Kamp M., Emmerling M., Forchel A., Prunnila M., Ahopelto J., Submitted to *Jpn. J. Appl. Phys.* (2000).

INTERSUBBAND ELECTRON SCATTERING RATES IN ONE-DIMENSIONAL Si MOS-STRUCTURE

V. M. BORZDOV, V. O. GALENCHIK, O. G. ZHEVNYAK, F. F. KOMAROV

*Belarusian State University, Department of Radio-Physics and Electronics
220064 Minsk, Belarus*

E-mail: bvm@rfe.bsu.unibel.by

The intersubband electron scattering rates in one-dimensional Si MOS-structure are calculated. The results obtained are in a good agreement with known theoretical insight.

It is known that one of the ways to increase the silicon IC switching frequency is the use of new type of device structures with high electron mobility. An application of Si MOSFETs with one dimensional (1D) electron gas is very promising for this purpose. Though experimental samples of these structures were fabricated in early 80 s [1], some questions on the electron drift in such structures are not clear up to date. First of all, this is concerned with electron scattering processes in general and with intersubband transitions in particular.

One of the chief difficulties in evaluation of intersubband scattering rates in 1D Si MOS-structures is the need to calculate energy levels and wave functions. It is necessary to solve the two-dimensional Schrödinger equation for an unspecified form of quantum well with account the effective mass anisotropy.

The purpose of this work is the numerical calculation of intersubband scattering rates in 1D Si MOS-structure analogously with [1]. Assuming that the x-axis of Cartesian coordinates is directed along the structure channel the electron wave functions can be presented as

$$\Psi_{mn}(x, y, z) = A \cdot \exp(-ikx) \cdot \psi_{mn}(y, z), \quad (1)$$

where m and n are the quantum numbers, A is the scaling constant, k is the electron wave vector absolute value, ψ_{mn} is the envelope wave function. This function can be obtained from the numerical solution of the Schrödinger equation

$$-\frac{\hbar^2}{2} \left[\frac{1}{m_y} \frac{\partial^2}{\partial y^2} + \frac{1}{m_z} \frac{\partial^2}{\partial z^2} \right] \psi_{mn}(y, z) + e\varphi(y, z) \psi_{mn}(y, z) = E_{mn} \psi_{mn}(y, z), \quad (2)$$

where m_y and m_z are the effective masses in the direction y and z, respectively, e is the electron charge, E_{mn} is the (m,n) subband energy, $\varphi(y, z)$ is the electrostatic potential. It is necessary to take into account that three subband ladders with different m_y and m_z are formed in 1D electron gas according to the MOS-structure orientation [2]. In this work orientation of x-axis is chosen along <100> direction.

We derived the formulae for calculation of intersubband scattering rates using the results of [3] and supposed that parabolic approximation is valid.

The intersubband acoustic phonon scattering rate from subband (m,n) to subband (m',n') is evaluated according to the expression

$$W_{mm'n'}^{ac} = \sqrt{\frac{2m_d}{E_{mn} + E - E_{m'n'}}} \frac{D_{ac}^2 k_b T g_{m'n'}}{\rho \hbar^2 s^2} U(E_{mn} + E - E_{m'n'}) \times \int |\psi_{mn}(y, z) \psi_{m'n'}(y, z)|^2 dy dz, \quad (3)$$

where m_d is the density-of-state effective mass, D_{ac} is the deformation potential of acoustic phonon scattering, k_b is the Boltzmann constant, T is the crystal temperature, ρ is the mass density, s is the sound velocity, U is the step function, E is the kinetic energy, $g_{m'n'}$ is the final state degeneracy.

The intersubband optic phonon scattering rate from subband (m,n) to subband (m',n') is calculated according to the formula

$$W_{mm'n'}^{opt}(E) = \sqrt{\frac{m_d}{2(E_{mn} + E \mp k_b T_{ph} - E_{m'n'})}} \frac{D_{opt}^2 g_{m'n'}}{\rho k_b T_{ph}} \left(N_{ph} + \frac{1}{2} \pm \frac{1}{2} \right) \times \\ \times U(E_{mn} + E \mp k_b T_{ph} - E_{m'n'}) \int |\psi_{mn}(y, z) \psi_{m'n'}(y, z)|^2 dy dz, \quad (4)$$

where D_{opt} is the coupling constant, N_{ph} is the population of phonons with temperature T_{ph} . Upper sign corresponds to phonon emission, lower one does to phonon absorption.

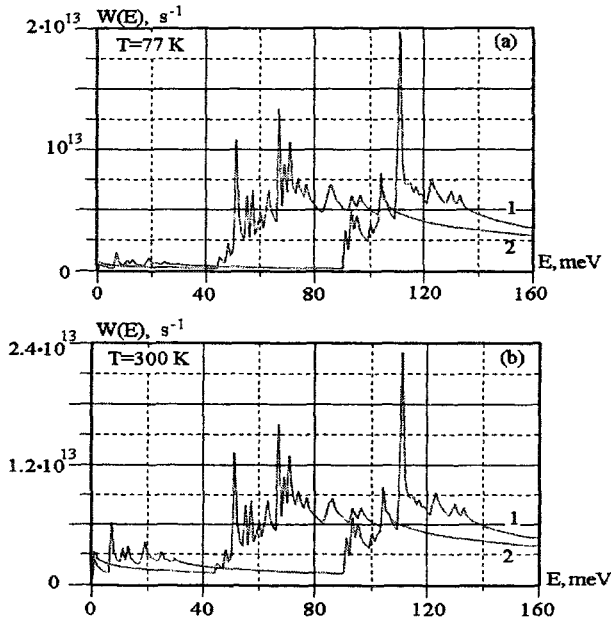


Figure 1. The sum of the phonon scattering rates from the lowest subband (curve 1) and the highest subband (curve 2) versus kinetic energy E at 77 K (a) and 300 K (b). The transverse electric field in MOS-structure is equal to 10^6 V/m.

In Fig. 1 the sum of the phonon scattering rates from the lowest and highest subbands are plotted against kinetic energy at different temperatures. We considered 27 subbands. Both backward and forward scattering were taken into account. The temperature growth increases scattering rates. The stepwise character of $W(E)$ is determined by the electron energy quantization. The presence of the peaks on the curves can be explained by peculiarities of the density of states in 1D electron gas.

In conclusion, we obtained formulae and calculated the intersubband scattering rates in 1D electron gas. The results obtained are in good agreement with known theory [4].

References

1. Skocpol W., Jackel L., Howard R., Mankevich P., Tennant D., White A., Dynes R., Quantum transport in narrow MOSFET channels, *Surf. Sci.* **170** (1986) pp. 1–13.
2. Laux S., Stern F., Electron states in narrow gate induced channels in Si, *Appl. Phys. Lett.* **49** (1986) pp. 91–93.
3. Calecki D., Electron distribution function and inelastic scattering in one- and two-dimensional structures, *J. Phys. C: Solid State Phys.* **19** (1986) pp. 4315–4328.
4. Mickevičius R., Mitin V., Acoustic-phonon scattering in a rectangular quantum wire, *Phys. Rev. B* **48** (1993) pp. 17194–17201.

THE POTENTIAL OF β -FeSi₂ NANOSTRUCUTRES FOR SOLAR CELL APPLICATIONS

C. N. MCKINTY, K. J. KIRKBY, K. P. HOMEWOOD

*University of Surrey, School of Electronic Engineering, Information Technology & Maths
Guildford, United Kingdom*

S.-P. EDWARDS, G. SHAO

*University of Surrey, School of Mechanical & Materials Engineering
Guildford, United Kingdom*

R. VALIZADEH, J. S. COLLIGON

*Department of Chemistry & Materials, Manchester Metropolitan University
Manchester, United Kingdom*

E-mail: C.Mckinty@ee.surrey.ac.uk

β -FeSi₂ has been shown to have a minimum direct band gap of 0.87 eV [1], with a large absorption coefficient above the fundamental edge (10^5 cm^{-1}) [2]. In this paper we report the formation of β -FeSi₂ by co-sputtering of Fe and Si, for the use in solar cell applications.

1 Introduction

The formation of β -FeSi₂ has been achieved by many techniques, these have included ion beam synthesis and ion beam assisted deposition (IBAD). A detailed review of this material system has been produced by Lange et al. [3].

IBAD offers a cheap method of depositing layers of a variety of materials for large area applications. β -FeSi₂ has a minimum direct band gap of 0.87 eV [1] with a large absorption above the fundamental edge (10^5 cm^{-1}) [2]. Predicted solar cell efficiencies have been put as high as 23 % [4], while an investigation of the photoelectric properties have shown a photoelectric quantum efficiency of 32 % [5]. IBAD β -FeSi₂ thus has great potential as a material for solar cell applications.

In this paper we outline the suitability of IBAD β -FeSi₂ as a potential material for solar cell applications.

2 Methods

Si [100] n-type substrates were coated with films containing a mixture of Fe and Si using IBAD method. A detailed explanation of the fabrication process can be found elsewhere [6]. Subsequently the samples were annealed in a nitrogen ambient for

various times and temperatures. Previous publications have concentrated on a range of Fe:Si ratios [6]; the work reported here concentrates on the deposition of Fe:Si in stoichiometric ratios. A 600 nm layer of Si and Fe was deposited onto an n-type substrate in the ratio Si:Fe (2:1), and then capped with 100 nm of Si.

The magnitude and nature of the optical band gap was determined by optical absorption measurements made in transmission, a more detailed explanation of this technique can be found elsewhere [6].

Solar cell test structures were fabricated by depositing a "finger" Al ohmic front contact (on the Si capping layer) and an AuSb ohmic back contact (on the substrate). Samples annealed at 800 °C for 20 min and 900 °C for 18 h, respectively, were investigated. The resulting structure forms a p-n junction, as β -FeSi₂ has been reported to be p-type when deposited by co-deposition techniques [5]. The photovoltage generated by each sample (illuminated by a chopped white light source) was measured by a lock-in amplifier. By passing the light through a spectrometer before illuminating the sample, it was also possible to investigate the spectral response of the devices.

3 Results

Annealing was found to have a major effect on the samples: no band gap was detected with optical absorption until the annealing temperature was increased to 475 °C. This indicated that β -FeSi₂ formation occurred around 475 °C. Increasing the temperature above 800 °C was shown to cause the morphology of the layers to deteriorate. This is illustrated in Fig. 1, which show cross-sectional transmission electron microscopy (X-TEM) images for samples as-deposited and annealed at 900 °C for 18 h, respectively.

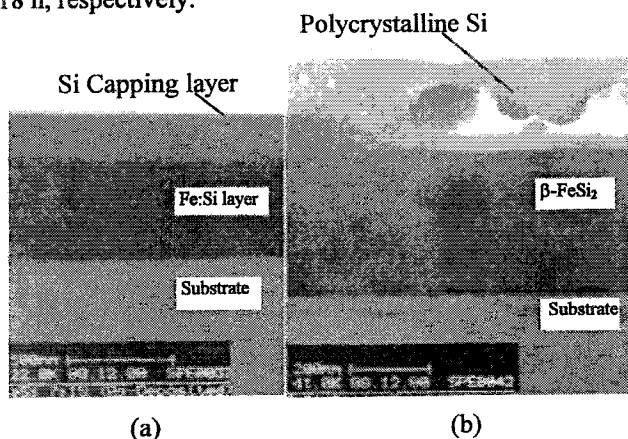


Figure 1. X-TEM images of samples (a) as-deposited and (b) annealed at 900 °C for 18 h in a nitrogen ambient.

The β -FeSi₂ layer shown in Fig. 1(b) exhibits an orientation relationship (OR) with the substrate (determined from a selected area diffraction pattern not shown), which is close to the type-I OR [7]. This type-I OR is characterised with a small lattice mismatch with the Si substrate. The top Si layer was transformed into polycrystalline Si after annealing at 900 °C (the as-deposited Si was amorphous). The pores in the polycrystalline Si layer could be attributed to the Kirkendall effect [8] due to the intermixing of the amorphous Si with the as-deposited Fe:Si layer.

All the solar cell devices fabricated on samples annealed at 800 °C for 20 min and 900 °C 18 h exhibited rectifying I-V characteristics (not shown). A photovoltage was also generated by each sample when illuminated. Preliminary results from measuring the spectral response of the devices indicate that the photo voltage is generated at both the β -FeSi₂ and Si band edges, though further work is necessary to ascertain the individual components.

4 Discussion

The results reported here confirm that β -FeSi₂ offers a novel route for achieving the photovoltage generation. There are still many fabrication issues that need to be overcome, which include quality of Si/ β -FeSi₂ interface and stability of the layers. However, it is apparent that if these issues can be overcome the realisation of the high efficiencies for β -FeSi₂ solar cells [4] is feasible.

References

1. Hunt T. D., Reeson K. J., Homewood K. P., Teon S. W., Gwilliam R. M., Sealy B. J., *Nucl. Instrum. Meth. Phys. Res. B* **84** (1994) 168.
2. Yang Z., Homewood K. P., Finney M. S., Harry M. A., Reeson K. J., *J. Appl. Phys.* **78** (3) (1995).
3. Lange H., *Phys. Stat. Sol. (b)* **201** (1997) 3.
4. Powalla M., Herz K., *App. Sur. Sci.* **65/66** (1993) 482.
5. Maeda Y., Miyake K., Ohashi K. In *Proceeding of Japan-UK Joint workshop on Kankyo-Semiconductors* (Japan, 2000).
6. McKinty C. N., Kewell A. K., Sharpe J. S., Lourenco M. A., Butler T. M., Valizadeh R., Colligon J. S., Reeson K. J., Kirkby K. J., Homewood K. P., *Nucl. Instrum. Meth. Phys. Res. B* **161-163** (2000) 922.
7. Shao G., Homewood K. P., *Intermetallics* **8** (2000) 1405.
8. Cottrell A., *An introduction to Metallurgy*.

RESONANT TUNNELING THROUGH AN ARRAY OF QUANTUM DOTS COUPLED TO SUPERCONDUCTORS UNDER THE EFFECT OF MAGNETIC FIELD

A. N. MINA

*Faculty of Science, Cairo University, Beni-Suef Branch
Beni-Suef, Egypt*

E-mail: adelphil@aucegypt.edu

Quantum transport characteristics of an array of semiconductor quantum dots coupled to superconducting leads are studied under the effect of magnetic field. The conductance of this mesoscopic device was deduced by solving the Bogoliubov-de Gennes (BdG) equation. The energy dependence of the normalized conductance show a resonance behavior for different transparency of the superconductor (S) - semiconductor (S_m) interface. The magnetic field dependence of the conductance shows quantization in units of $2 e^2/h$ with resonance.

1 Introduction

Quantum transport in mesoscopic structures of metals, semiconductors, and superconductors has been of considerable interest for more than a decade [1,2]. Quantum dots [3] can be weakly coupled via tunnel barriers to external leads in order to study their transport properties. For sufficiently low temperatures the conductance of the dot exhibits equally spaced peaks with increasing gate voltage [4-6] where each successive peak corresponds to a tunneling of a single electron into the dot. This occurs when the increase in the Fermi energy in the leads matches the energy required to charge the dot by one additional electron. The suppression of tunneling between the peaks by Coulomb repulsion is known as Coulomb blockade [7].

Recently, the conductance of a NbN-2DEG-NbN junction [8] was measured experimentally under the effect of a magnetic field. Their results show a quantization of the conductance of the junction.

In the present paper, a model for an array of quantum dots coupled to a superconducting leads is proposed. The quantum transport characteristics of this mesoscopic device are studied under the effect of a magnetic field.

2 Theoretical treatment

Mesoscopic device, in this paper, can be modeled as array of semiconductor quantum dots coupled weakly to two superconducting leads via tunnel barriers. The conductance of this device is given by [9]:

$$G = \frac{e^2 k_F^2}{4\pi^2 \hbar} T, \quad (1)$$

where k_F is the Fermi wave vector, $\hbar$ is the reduced Planck's constant, e is the electronic charge and T is the tunneling probability. We deduce an expression for the tunneling probability, T , by solving the Bogoliubov-de Gennes (BdG) equation [10]

$$\begin{pmatrix} H & \Delta \\ -\Delta & H^* \end{pmatrix} \psi = E \psi, \quad (2)$$

where the Hamiltonian H of the system is given by:

$$H = -\frac{\hbar^2}{2m^*} \frac{d^2}{dx^2} + V_j + \frac{U_c N^2}{2} + \hbar \omega_c - E_F, \quad (3)$$

where V_j is the potential barrier height at the j -th region of the quantum dot, U_c is the charging energy of the quantum dot, E_F is the Fermi energy, Δ is the superconductor energy gap. The magnetic energy is given by $\hbar \omega_c = \hbar \frac{eB}{m}$, where B is the magnetic field. The solution of (2) is

$$\psi_j(x) = A_j \exp(ik_j x) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + B_j \exp(-k_j x) \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (4)$$

This eigenfunction is inside the quantum dot in the j -th region and the corresponding eigenfunction inside the superconducting leads is given by:

$$\psi(x) = C \exp(ik'x) \begin{pmatrix} u \\ v \end{pmatrix} + D \exp(-ik'x) \begin{pmatrix} v \\ u \end{pmatrix}. \quad (5)$$

The wave vector inside j -th quantum dot is

$$k_j = (2m^*(V_{\text{eff}} \pm E))^{0.5} / \hbar, \quad (6)$$

where

$$V_{\text{eff}} = V_0 + \frac{U_c N^2}{2} + \hbar \omega_c + E_F, \quad (7)$$

and the corresponding wave vector of quasiparticles inside each superconductor is

$$k' = (2m^*(E_F - V_0 \pm \sqrt{E^2 - \Delta^2}))^{1/2} / \hbar. \quad (8)$$

The eigenfunction u , v of the corresponding quasiparticles (electrons/holes) due Andreev reflection process which occurs at the S-Sm interface are given by:

$$u = \sqrt{\frac{1}{2} \left(1 + \frac{(E^2 - \Delta^2)^{0.5}}{E} \right)} \quad v = \sqrt{\frac{1}{2} \left(1 - \frac{(E^2 - \Delta^2)^{0.5}}{E} \right)}.$$

The coefficients A_j and B_j are determined by matching conditions at the S-Sm interface, that is

$$\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = \prod_{j=1}^6 R_j \begin{pmatrix} A_7 \\ B_7 \end{pmatrix}, \quad (9)$$

where the coefficient R_j is expressed as follows:

$$R_j = \frac{1}{2k_j} \begin{pmatrix} (k_j + k_{j+1}) \exp(i(-k_j + k_{j+1})x_j) & (k_j - k_{j+1}) \exp(i(-k_j - k_{j+1})x_j) \\ (k_j - k_{j+1}) \exp(i(k_j + k_{j+1})x_j) & (k_j + k_{j+1}) \exp(i(k_j - k_{j+1})x_j) \end{pmatrix}. \quad (10)$$

It can be shown that the tunneling probability T is expressed as [12]:

$$T = (1 + C_1^2 C_2^2)^{-1}, \quad (11)$$

where

$$C_1 = \frac{(V_{\text{eff}} \cdot \sinh kb)}{2\sqrt{E(V_{\text{eff}} - E)}}, \quad (12)$$

$$C_2 = 2 \cosh(kb) \cdot \cos(k'a) - \left(\frac{(2E - V_{\text{eff}})}{(E(V_{\text{eff}} - E))} \right) \exp(2kb) \cdot \frac{\sin(k'a)}{2}. \quad (13)$$

The parameters a and b represent the diameter of the quantum dot and the width of the barrier.

Now, substituting (12,13) into (11) we get an expression for the tunneling probability T . It is then substituted into (1) to get the conductance G for the junction considered in this paper

$$G = \frac{e^2 k_F^2}{4\pi^2 \hbar} (1 + C_1^2 C_2^2)^{-1}. \quad (14)$$

3 Numerical calculations

The Schottky barrier height at the S-Sm interface was determined as previously [13]. The conductance was calculated at different magnetic fields, bias voltage and the energy of electrons.

Fig. 1 shows the normalized conductance-energy relation which exhibits a resonance behavior. This might be due to quantum interference of quasiparticles under the effect of magnetic field. This result is in good agreement with those in the literature [11].

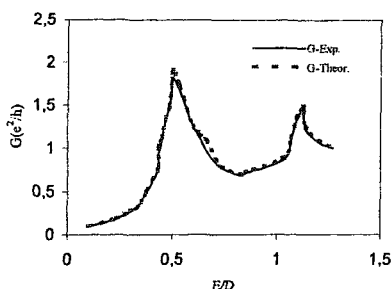


Figure 1. Energy dependence of conductance.

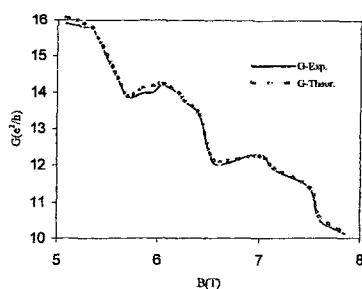


Figure 2. Magnetic field dependence of the conductance.

Fig. 2 shows the conductance-magnetic field relation. This relation exhibits a quantization in the conductance as predicted experimentally in [8].

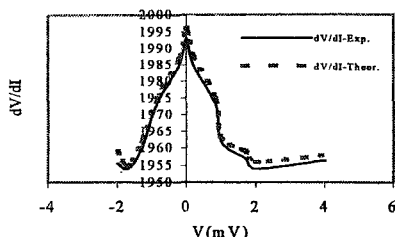


Figure 3. voltage dependence of differential resistance.

Fig. 3 shows the differential resistance-bias voltage relation which exhibits a peak at $V=0$. The present results are in good agreement with those [8]. These results show the role of Andreev reflection between two NbN-2DEG interface and accordingly subharmonic energy gap structure should appear at $V = 2\Delta/(ne)$, ($n = 1, 2, \dots$). In case of NbN, the energy gap $\Delta \sim 3$ meV, i.e., in our case $n = 2$ which agrees with [8,14].

4 Conclusion

In the present paper, the conductance of the mesoscopic device was derived by solving the Bogoliubov-de Gennes equation. It was found a quantization of conductance with resonance at certain values of energy. Our results are in good agreement with those in the literature.

References

1. Beenakker C. W. J., *Mesoscopic Quantum Physics* (North-Holland, Amsterdam, 1995).
2. van Wees B. J., Takayanagi H., *Mesoscopic Electron Transport* (Kluwert, Dordrecht, 1997).
3. Kastner M. A., *Rev. Mod. Phys.* **64** (1992) 849.
4. Legand B., et al., *Appl. Phys. Lett.* **73** (1998) 96.
5. Phillips J., et al., *Appl. Phys. Lett.* **72** (1998) 3509.
6. Kutchinsky J., et al., *Phys. Rev. Lett.* **78** (1997) 931.
7. Kashiway S., et al., *Jpn. J. Appl. Phys.* **34** (1995) 4555.
8. Takayanagi H., et al., *Physica B* **249-251** (1998) 462.
9. Zaitsev A., *Sov. Phys. JETP* **59** (1984) 1115.
10. de-Gennes P. G., *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).
11. Khlus V. A., et al., *Physica C* **214** (1993) 413.
12. Claughton N. R., et al., *J. Phys.: Condens. Matter* **7** (1995) 8757.
13. Mina A. N., Phillips A. H., Shaheen M. F., Said N. A., *Physica C* **341-348** (2000) 301.
14. Zyuzin A. Yu., *Phys. Rev. B* **50** (1994) 323.

MODELING OF THE DIFFERENTIAL CONDUCTANCE OF MESOSCOPIC SYSTEM: THEORY AND SIMULATION

A. H. ALY

*Physics Department, Faculty of Sciences, Cairo University
Beni-Suef, Egypt*

E-mail: arafal6@yahoo.com

Quantum conductance properties of a mesoscopic device are studied. The device is composed of a semiconductor between two superconducting electrodes. The results show the importance of the differential conductance measurements in order to get information about the subgap structure.

1 Introduction

Modern device fabrication techniques have made it possible to construct tunnel junction devices on the submicron level [1]. Such mesoscopic devices are the step in evolution of small devices whose primary objectives are faster characteristic times and a low energy dissipation. New effects rise in this mesoscopic domain as a result of the quantum mechanical phase of electrons as well as the discrete nature of the electronic charge. The quantized conductance explained by the Landauer formula [2] has been observed in [3,4].

The behavior of superconducting field-effect transistors is sensitive to the quality of the superconductor-semiconductor (S-Sm) contacts, and it is possible to change the carrier concentration in the semiconductor by the proximity effect.

In this paper a quantitative theory of the transport characteristics of the S-Sm-S sandwich type junction is developed. The role of the Andreev-reflection at the S-Sm interface is taken into account.

2 Theoretical approach

The junction under investigation, is S-Sm-S, where the semiconductor region is of mesoscopic size [5]. A Sm-S junction is convenient in manufacturing microelectronics devices, since the Schottky barrier at the interface is much more transparent than a typical dielectric tunnel barrier [6]. However, some semiconductors such as InAs do not form a Schottky barrier at the S-Sm interface. At this interface electrons experience two processes, namely, normal tunneling and Andreev reflection [7]. We will compute the conductance G for both process.

The conductance, G_1 , due to the normal tunneling of electrons is given by [8]:

$$G_1 = \frac{2e\Delta^2}{\hbar} \int_{E_F}^{E_F+2\Delta} dE \left(-\frac{\partial f}{\partial E}\right) |\Gamma|^2 \sin \varphi, \quad (1)$$

where $-\frac{\partial f}{\partial E}$ is the derivative of the Fermi-Dirac function, k_B is Boltzman constant, E_F is Fermi energy, Δ is the superconductor energy gap, φ , is the phase angle, Γ is the tunneling probability of an electron through the Schottky barrier. The latter could be determined by the WKB method [9]:

$$\Gamma = \exp\left[-\frac{2}{\hbar} \int [2m(U(x) - E)]^{1/2} dx\right], \quad (2)$$

where the potential $U(x)$ is given by [9]:

$$U(x) = q\phi_b + 2\Delta - \frac{q^2 N_B}{\epsilon} \left(wx - \frac{x^2}{2} \right) - \frac{q^2}{16\pi\epsilon x}, \quad (3)$$

the depletion layers w is

$$w = \left[\frac{2\epsilon(\phi_b - V_o)}{eN_B} \right]^{1/2}, \quad (4)$$

where ϕ_b is the Schottky barrier height, N_B is the semiconductor doping density, ϵ is the permittivity of the semiconductor, q is the electronic charge and V_o is the bias voltage. The term $q^2/16\pi\epsilon x$ in (3) represents the image force.

Now, substituting (3) into (2), taking into account (4) and performing the integration we get the tunneling probability Γ . After substituting it into (1) and performing the integration we finally get:

$$G_1 = \frac{q\Delta^2 \hbar^2}{K_B T \hbar V_o} (\sin \varphi_1) \ell n \frac{(1 + \exp(\frac{E_F - 2\Delta}{k_B T}))}{(1 + \exp(\frac{E_F + qV_o}{k_B T}))} \exp\left[-\frac{2\sqrt{2m^*q}}{\hbar} \left\{ 2\Delta + (\phi_b - V_o) + \left(\frac{q\pi\sqrt{N_B}}{\epsilon} \right)^{1/2} D \right\} \right]. \quad (5)$$

The tunneling probability Γ depends on ϕ_b , N_B , ϵ , and the distance between the two electrodes D .

The differential conductance G_2 due to Andreev reflection [8,9] could be calculated as follows. At the S-Sm interface the dissipative electrical current is converted into the dissipationless supercurrent. The mechanism for this conversion was discovered by Andreev [12]. An electron excitation slightly above the Fermi level in the semiconductor is reflected at the interface as a hole excitation slightly below the Fermi level. The missing charge $2q$ is removed as a supercurrent. The reflected hole has (approximately) the same momentum as the incident electron. This curious scattering process is known as the Andreev reflection. So, the conductance G_2 will be computed using the relation:

$$G_2 = (1/eR_n V_o) \int A(E) f(E - qV_o) dE, \quad (6)$$

where $R_n = (1 + 2Z^2)R_0$, and $R_0 = [2Ae^2 v_F N(0)]^{-1}$, in which Z , A , v_F , and $N(0)$ are respectively, the dimensionless scattering parameter modelling the elastic scattering at the S-Sm interface, the cross-sectional area of the interface, the Fermi velocity,

and the density of states at the Fermi energy. The parameter $A(E)$ represents the probability of the Andreev reflection at the S-Sm interface [7,11]:

$$A(E) = [2(E^2 - \Delta^2)^{1/2}] / [E + (E^2 - \Delta^2)^{1/2}] \quad (7)$$

Now, substituting (7) into (6) and performing integration, we get an expression for the Andreev reflection contributed part of the differential conductance:

$$G_2 = \left(\frac{1}{qV_0 R_n} \right) \left[\frac{2E(qV_0 + E_F)}{(k_B T)^2} \right] \cosh^{-1} \frac{E}{\Delta + qV_0} \bigg|_{E_{\min}}^{E_{\max}}, \quad (8)$$

where the limits $E_{\min}$ and $E_{\max}$ are the minimum and maximum energies of electrons in the Andreev reflection at the S-Sm interface. The total differential conductance G of the junction under study is a sum of two contributions: from the normal tunneling process (5) and from the Andreev reflection process (8).

3 Results and conclusion

We have calculated the total differential conductance G , considering the tunneling process as a stochastic one. The values of energies of the tunnelling electrons and these of the electrons which experience the Andreev reflection has been varied as a random variable and we calculated the values of $E_{\min}$ and $E_{\max}$ by the Monte-Carlo technique. Also, we calculated the barrier height, ϕ_b to be 0.53 eV. This value is in good agreement with [12]. Figs. 1,2 present results showing variation of the differential conductance G with V_0 .

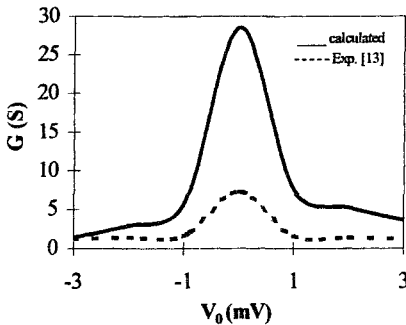


Figure 1. Bias voltage dependence of the differential conductance at $\phi_b = 0$.

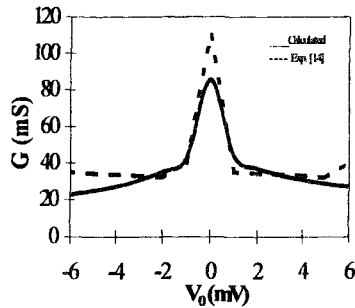


Figure 2. Bias voltage dependence of the differential conductance at ϕ_b considered.

Fig. 3 shows the decrease of the differential conductance G with the temperature increase.

In conclusion, the quantum transport in the S-Sm-S mesoscopic system has been treated on the basis of the WKB approximation and taken into consideration the role of the Andreev reflection. The final formula for the current has been deduced. The numerical results obtained are found to be in fair agreement with the experimental data.

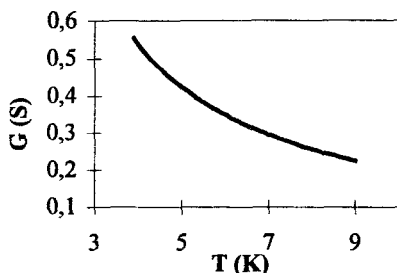


Figure 3. Temperature dependence of the differential conductance.

References

1. Averin D. V., Likharev K. K. In *Nanostructures and Mesoscopic systems*, ed. by Kirk W. P., Reed M. A. (Academic Press, Boston, 1992).
2. Landauer R., *Phil. Mag.* **21** (1970) 863.
3. Van Wees B. J., Van Houten H., Beenakker C. W. J., Williamson J. G., Kouwenhoven L. P., Van der Marel D., Foxon C. T., *Phys. Rev. Lett.* **60** (1988) 848.
4. Wharam D. A., Thornton T. J., Newbury R., Pepper M., Ahmed H., Frost J. E. F., Hasko D. G., Peacock D. C., Ritchie D. A., Jones G. A., *J. Phys. C* **21** (1988) L209.
5. Klapwijk T. M., *Physica B* **197** (1994) 481.
6. Beenakker C. W. J. In *Transport Phenomena in Mesoscopic Systems*, ed. by Fukuyama H., Ando T. (Springer, Berlin, 1992).
7. Blonder G. E., Tinkham L., Klapwijk T. M., *Phys. Rev. B* **52** (1982) 451.
8. Glazman L. I., Lesovik G. B., Khmel'ntskii D. E., Shekhter R. I., *JETP Lett.* **48** (1988) 238.
9. Aly H. A., *Ph. D. Thesis* (1999).
10. Beenakker C. W. J. In *Mesoscopic Quantum Physics*, ed. by Akhmanov E. et al. (North-Holland, Amsterdam, 1995).
11. Andreev A. F., *JETP* **19** (1964) 1228.
12. Becker Th., Muck M., Heidenet Ch., *Physica B* **204** (1995) 183.
13. Kroemer H., Nguyen C., Hu E. L., Yuh E. L., Thomas M., Wong Ki C., *Physica B* **203** (1994) 298.
14. Kleinsasser A. W., Jackson T. N., McInturff D., Rammo F., Petti G. D., Woodall J. M., *Appl. Phys. Lett.* **57** (1990) 1812.

This page is intentionally left blank

AUTHOR INDEX

- Adamson P., 208
 Ahopelto J., 182, 473
 Aktsipetrov O. A., 196
 Akulov G. Y., 389
 Aleshkin V. Ya., 138
 Aly A. H., 487
 Andreev B. A., 466
 Angrisani Armenio A., 250
 Anishchik V. M., 389
 Arnaud d'Avitaya F., 437, 461
 Artemyev M. V., 152, 412
 Astafiev O., 466
 Attanasio C., 250
- Balk L. J., 212
 Bassani F., 200, 437
 Bauer E., 228
 Bayer M., 30
 Bechstedt F., 158, 162
 Belich R. F., 428
 Belogorokhov A. I., 320
 Belogorokhova L. I., 320
 Belous I. A., 186
 Berashevich J. A., 470
 Berbezier I., 57
 Bibik A. I., 48, 102
 Bimberg D., 147
 Biryukov A. V., 138
 Bogdanchikova N. E., 284
 Bogdanov E. V., 130
 Bogush V., 432
 Bokshits Yu. V., 290
 Bondarenko A. S., 311
 Borisenko V. E., 3, 212
 Born H., 147
 Borzdov V. M., 477
 Buhmann H., 40
 Butler T. M., 76
- Carmo M. C., 147
 Caruso F., 298
 Caruso R. A., 298
 Cavaco A., 147
 Cepek C., 94
 Chang Y. P., 379
 Cichos F., 302
 Colligon J. S., 480
- Danil'tsev V. M., 138
 Danilyuk A. L., 461, 470
 Dmitriev A. V., 110, 122
 Dolgova T. V., 196
 Dzero M. O., 48
- Edamatsu K., 22
 Edwards S.-P., 480
 Efremov A. A., 416
 Efremov M. D., 126, 134
 Emmerling M., 473
 Erofeeva I. V., 466
 Evtukh A. A., 416
 Eychmuller A., 307
- Fedin D. V., 416
 Fedorov I., 394
 Fedorovich R. D., 276
 Fedoruk G. G., 204
 Fedutik Yu. A., 290
 Fedyanin A. A., 196
 Feshchenko D. V., 428
 Forchel A., 30, 473
 Forró L., 86
 Furthmüller J., 158, 162
- Gaiduk P. I., 375

- Galaktionov E. A., 126, 134
 Galenchik V. O., 477
 Galkin K. N., 192
 Galkin N. G., 192, 246
 Gaponenko N. V., 216, 397
 Gaponenko S. V., 118, 216
 Gaponik N. P., 307
 Gaponov S. V., 138
 Gavrilenko V. I., 466
 Gavrilov S. A., 316, 320
 Gerlach B., 48
 Glybin V., 432
 Goroshko D. L., 246
 Grundmann M., 147
 Grushevski V. V., 389
 Guirleo G., 200
 Gurin V. S., 284
 Gurinovich L. I., 152
 Gusyatnikov V. N., 142
- Hansen O. P., 130
 Heiderhoff R., 212
 Heinrichsdorff F., 147
 Heitz R., 147
 Heuken M., 384, 455
 Hiyamizu S., 22
 Hoffmann A., 147
 Homewood K. P., 76, 480
- Ichikawa M., 356
 Ilievsky A. A., 130
 Ilyushonok I. P., 324
 Ioannou-Sougleridis V., 437
 Itoh T., 22
- Jalochowski M., 228
- Kachan S. M., 238
 Käckell P., 162
- Kaganovich E. B., 174, 178
 Kamp M., 473
 Kassing R., 332
 Kawabe M., 15
 Kawano Y., 466
 Kazak N. S., 421
 Keiper R., 110
 Khilo A. N., 421
 Khmelnitski A. I., 389
 Kholod A. N., 461, 472
 Khrykin O. I., 138
 Kirkby K. J., 76, 480
 Kislyakov E. F., 204
 Kivinen P., 182, 473
 Kiyayev O. E., 276
 Klyui N. I., 170
 Kolesnik E. E., 407
 Komarov F. F., 477
 Komiyama R. S., 466
 Kononenko V. K., 142
 Korneta O. B., 170
 Korotkov A. L., 466
 Koshikawa T., 228
 Kosikov S. I., 192
 Kraak W., 130
 Krachino T. V., 166
 Kravtchenko D. A., 320
 Kretinin A. V., 134
 Krivoshchapov S. Ts., 246
 Krylova G. V., 389
 Kudrawiec R., 224
 Kukhareno L. V., 389
 Kukhta A. V., 407
 Kushnir V. N., 250
 Kuz'min M. V., 166
- Lavrinenko A. V., 118
 Lazarouk S. K., 446
 Lee B. C., 379
 Lee C. P., 379
 Lee H. M., 379
 Lemesko S. V., 316

Leschenko V. G., 389
 Lifshits V. G., 186
 Liniger M., 203, 461
 Litovchenko V. G., 170, 416
 Litvin Yu. M., 416
 Loginov M. V., 166
 Lourenco M., 76
 Luenenbuerger M., 384, 455
 Lundsgaard Hansen J., 375
 Lutsenko E. V., 384, 455
 Lynkov L., 432

Makara V. A., 170
 Makeyev V. V., 110
 Maksimov S., 40
 Manninen A., 182, 473
 Manoilov E. G., 174, 178
 Maria Grazia Betti, 258, 264, 265
 Maritato L., 250, 367
 Marko I. P., 388, 455
 Marowsky G., 196
 Martemyanov M. G., 196
 Maslov A. M., 192
 Mattei G., 196
 Maydikovskii A. I., 196
 Mckinty C. N., 76, 480
 Metelskiy T. A., 428
 Miglio L., 69
 Milesenko L. P., 224
 Mina A. N., 483
 Minina N. Ya., 130
 Mironov V. L., 138
 Misevich A. V., 324
 Misiewicz J., 30, 224
 Mitianok V. V., 106
 Mittsev M. A., 166
 Möhwald H., 294
 Molchan I. S., 224
 Molenkamp L. W., 40
 Morozov Yu. A., 142
 Mudryi A. V., 216, 455
 Murel A. V., 138

Nassiopoulou A. G., 437
 Naumovets A. G., 276
 Nawrocki W., 242
 Nefedov I. S., 142
 Nylandsted Larsen A., 375

Ouisse T., 437
 Outkina E. A., 403

Pachinin V. I., 224
 Pavlovskii V. N., 388, 455
 Pekola J., 182, 473
 Petranovskii V. P., 284
 Petrov A. Yu., 250
 Piryatinskii Yu. P., 170
 Pivin J. C., 216, 401
 Pochtenny A. E., 324
 Poklonski N. A., 106, 204
 Ponyavina A. N., 238, 216
 Popov V. V., 114
 Portavoce A., 57
 Poznyak S. K., 307
 Preobrazhenskii V. V., 126, 134
 Prikhodko P., 394
 Prischepa S. L., 250
 Prokhorov O. A., 216
 Protzmann H., 384, 455
 Prunnila M., 182, 473
 Pupysheva O. V., 122

Radtchenko I. L., 294
 Ragoisha G. A., 311
 Raiteri P., 69
 Rassamakin Yu. V., 416
 Rogach A. L., 307
 Ronda A., 57
 Roschin V. M., 316
 Rozhin A. G., 170

Ryzhevich A. A., 421
Ryzhkov S. V., 186

Sachenko A. V., 174, 178
Sachkov V. A., 126, 134
Sagaidak D. I., 204
Sancrotti M., 94
Sandomirski K. S., 118
Sarikov A. V., 416
Savin A. M., 130
Savin A., 182, 473
Schineller B., 384, 455
Schönenberger C., 86
Schuhmacher D., 196
Schuster J., 302
Şek G., 30
Semyagin B. R., 126, 134
Sergeev O. V., 212
Shao G., 480
Shashkin V. I., 138
Shelekhina V. M., 216
Shevchenko G. P., 290
Shevyakov V. I., 316
Shevyakov V., 394
Shimomura S., 22
Shkorik N. A., 298
Shulga A. M., 266
Siaglo A. I., 106, 204
Skeldon P., 224
Smondyrev M. A., 48
Sobolev N. A., 147
Sorensen C. B., 130
Soukiassian P., 343
Stekolnikov A. A., 162
Stekolnikov A. F., 428
Stukalov O. M., 324
Stupak A. P., 216
Sukhorukov G. B., 294
Sun K. W., 379
Susha A. S., 298, 307
Svechnikov S. V., 178

Talanov A. O., 192
Talapin D. V., 307
Thomas P., 122
Thompson G. E., 224, 401
Thymbalov G. M., 114
Tomchuk P. M., 276
Tsukanov D. A., 186

Ushakov D. V., 142
Utas O. A., 186

Valentinotti F., 69
Valizadeh R., 480
Vityaz P. A., 216
Volodin V. A., 126, 134
Volpi F., 57
von Borczyskowski C., 266, 302
Vorobyova A. I., 403
Vostokov N. V., 138
Vyrko S. A., 106, 204

Watatani C., 22
Wawrzyniak M., 242
Weissker H.-Ch., 158
Woggon U., 152, 415
Wrachtrup J., 302
Wu J. C., 379

Yablonskii G. P., 384, 455
Yablonskiy A. N., 466
Yakovlev V. A., 196
Yasue T., 228

Zaslavsky A., 461
Zenkevich E. I., 266
Zhevnyak O. G., 477
Zhukov E. A., 320
Zhukovsky S. V., 118
Zubialevich V. Z., 455

www.worldscientific.com
4697 hc

ISBN 981-02-4618-8



9 789810 246181